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of the
SOCIETY OF DYERS AND COLOURISTS

Volume 70 Number 12

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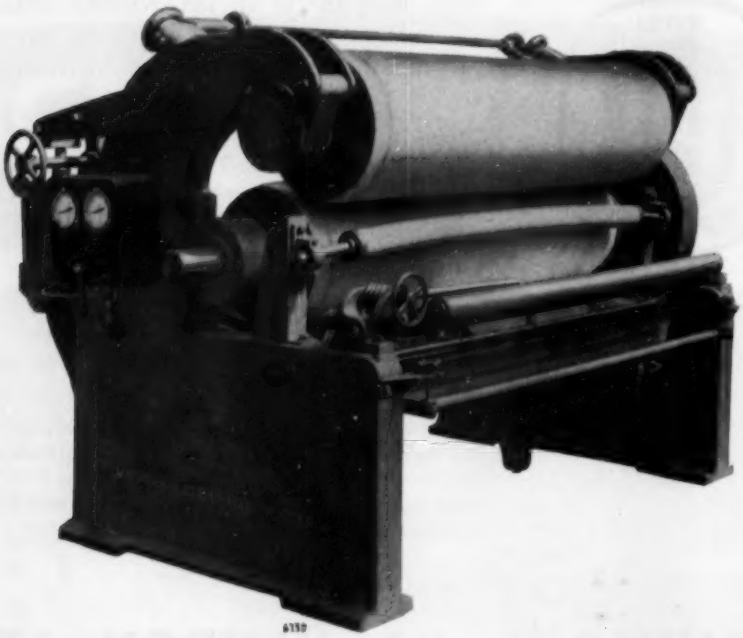

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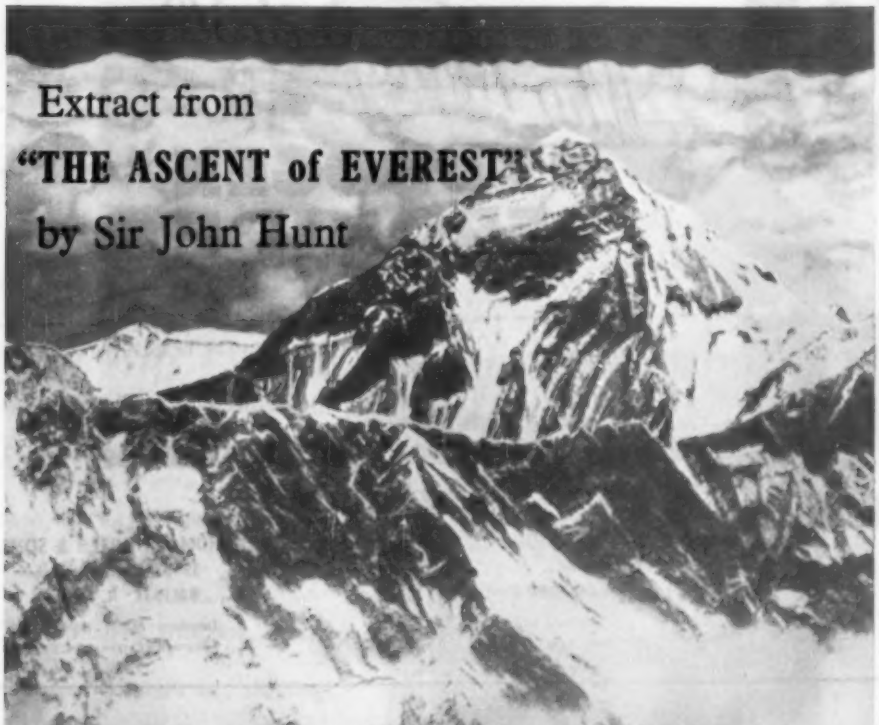

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NOTICE TO MEMBERS AND SUBSCRIBERS

Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc. should consult pages 1–6 of the January 1954 and pages 262–266 of the July 1954 issues of the *Journal*, or write to *The Secretary*, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire (*Telephone* Bradford 25138–9). *Editorial Communications* should be addressed to *The Editor*, at the same address.

Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

LECTURES

The Behaviour of Leuco Vat Dyes at Temperatures greater than 100°C. — *S. Blackburn and M. R. Fox*

Continuous Ribbon Dyeing — *L. J. Clarke*

The Basic Mechanisms of Dye Absorption during Pad Dyeing — *H. B. Mann*

Affinity Effects during Padding — *W. J. Marshall*

The Principles governing the Efficiency of a Padding Mangle — *H. Potter*

COMMUNICATIONS

The Influence of the Physical State of Dyes upon their Light Fastness — *G. Baxter, C. H. Giles, Miss M. N. McKee, and N. Macaulay*

The Dyeing of Acetate Rayon with Disperse Dyes
III—The Influence of Dispersing Agents on Rate of Dyeing — *Miss P. Harris, F. Manchester, and C. L. Bird*

The Polarography of Azo Dyes — *J. de O. Cabral and H. A. Turner*

The Mechanisms of Some Reactions between *N*-Halogenoamines and Wool — *C. Earland*

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FORTHCOMING MEETINGS OF THE SOCIETY

Thursday, 6th January 1955

NORTHERN IRELAND SECTION. *The Modern Approach to Linen Bleaching and Finishing* I. M. Hill, Esq. (Milltown Bleaching Co. Ltd.) (Joint lecture with Textile Institute). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Friday, 7th January 1955

LONDON SECTION. *Cellulose Acetate and Water Repellency.* R. J. Mann, Esq., B.Sc. (British Celanese Ltd.). Royal Society Rooms, Burlington House, **London, W.1.** 6 p.m.

Tuesday, 11th January 1955

BRADFORD JUNIOR BRANCH. Lecture. Title to be announced later (Messrs. S. Pegg & Son Ltd., Leicester).

Wednesday, 12th January 1955

NORTHERN IRELAND SECTION. *Application and Evaluation of Optical Bleaching Agents.* Messrs. G. G. Taylor, B.Sc., A.Inst.P., and G. Coe, A.M.C.T. (Clayton Dyestuffs Co. Ltd.). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Thursday, 13th January 1955

WEST RIDING SECTION. *Can Dyeing Theory Aid the Practical Dyer?* Dr. L. Peters (Department of Textile Industries, Leeds University). The Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Tuesday, 18th January 1955

HUDDERSFIELD SECTION. *Observations on the Dyeing of Wool at High Temperatures.* H. Sagar, Esq., A.T.I. (Imperial Chemical Industries Ltd.). The Co-operative Society Cafe, Buxton Road, **Huddersfield.** 7.30 p.m.

SCOTTISH SECTION. *Hydrogen Peroxide Bleaching in the Textile Industry.* Messrs. L. S. Chesner and B. A. Standish (Laporte Chemicals Ltd.). St. Enoch Hotel, **Glasgow.** 7 p.m.

Friday, 21st January 1955

MANCHESTER SECTION. Details later. Textile Institute. 6.30 p.m.

WEST RIDING SECTION. LADIES' EVENING. Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Tuesday, 25th January 1955

LEEDS JUNIOR BRANCH. *Some Observations on the Dyeing of Wool at High Temperatures.* H. Sagar, Esq., F.R.I.C., A.T.I. (Messrs. I.C.I. Ltd.). Departmental Lecture Theatre, The University, **Leeds.** 3.30 p.m.

Wednesday, 26th January 1955

MIDLANDS SECTION. *I do it this way!* Demonstrations of novel testing techniques by local members. College of Technology, **Leicester.** 7 p.m.

BRADFORD JUNIOR BRANCH. *Processing of "Dynel" Textiles.* D. H. Stott, Esq. (Gemec Chemical Company). **Bradford** Technical College. 7.15 p.m.

Thursday, 27th January 1955

WEST RIDING SECTION. *Some Aspects of Anthraquinone Dyestuffs Chemistry.* Dr. S. Coffey (Imperial Chemical Industries Ltd.). The Hotel Metropole, King Street, **Leeds.** 7.30 p.m.

Friday, 28th January 1955

LONDON SECTION. Annual Dinner Dance at The Waldorf Hotel, **London W.C.2.**

Tuesday, 1st February 1955

MANCHESTER JUNIOR BRANCH. *Rates of Uptake of Vat Dyes by Cellulose.* Dr. R. H. Peters and Dr. T. Watson (Messrs. I.C.I. Ltd.). College of Technology, **Manchester.** 6.30 p.m.

Friday, 4th February 1955

LONDON SECTION. *Textile Performance Standards for the Distributor.* Messrs. F. Cowles and J. S. Ingham (Marks and Spencer Ltd.). Royal Society Rooms, Burlington House, **London W.1.** 6 p.m.

Tuesday, 8th February 1955

MANCHESTER SECTION. Joint meeting with the Textile Institute in Macclesfield. *The Dyeing Properties of "Terylene" Polyester Fibre.* J. G. Graham, Esq., B.Sc. Fuller details later.

LEEDS JUNIOR BRANCH. *The Printing of Wool including the Production of Melange Effects.* J. A. Potter, Esq., M.A., F.S.D.C. (Messrs. Clayton Dyestuffs Co. Ltd.). Departmental Lecture Theatre, The University, **Leeds.** 3.30 p.m.

Wednesday, 9th February 1955

NORTHERN IRELAND SECTION. *Fastnesses of Coloured Textiles as they Affect the General Public.* J. S. Ingham Esq. (Marks & Spencer Ltd.). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Thursday, 10th February 1955

WEST RIDING SECTION. Details Later.

Tuesday, 15th February 1955

HUDDERSFIELD SECTION. *Non-Textile Uses of Dyestuffs.* J. P. Gill, Esq., B.Sc. (Imperial Chemical Industries Ltd.). Joint meeting with Huddersfield Section of the Royal Institute of Chemistry. The Co-operative Society Cafe, Buxton Road, **Huddersfield.** 7.30 p.m.

SCOTTISH SECTION. *pH in the Textile Industry.* T. Green, Esq., A.M.C.T. (Clayton Dyestuffs Co. Ltd.). St. Enoch Hotel, **Glasgow.** 7 p.m.

Friday, 18th February 1955

MANCHESTER SECTION. *The Soiling of Synthetic and Natural Fibres.* G. G. Taylor, Esq., B.Sc., A.Inst.P. (Clayton Dyestuffs Co. Ltd.). Textile Institute. 6.30 p.m.

Monday, 21st February 1955

BRADFORD JUNIOR BRANCH. Messrs. I.C.I. Ltd. and Petroleum Film Bureau. Film Evening.

Wednesday, 23rd February 1955

MIDLANDS SECTION. *The Classification of Dyestuffs by their Dyeing Characteristics.* W. Beal, Esq., B.Sc. Kings Head Hotel, **Loughborough.** 7 p.m.

Thursday, 24th February 1955

WEST RIDING SECTION. *Heat Sensitivity of Anthraquinone Acid Wool Dyes.* Dr. R. H. Peters and Dr. T. Watson (Messrs. I.C.I. Ltd.). The Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Friday, 25th February 1955

MANCHESTER SECTION. Annual Dance.

March 1955

LONDON SECTION. The London Lecture. Details later.

Tuesday, 1st March 1955

LEEDS JUNIOR BRANCH. *The Application of Azoic Dyes to "Terylene" Polyester Fibre at 100-130° C.* H. R. Hadfield, Esq., M.Sc. (Messrs. I.C.I. Ltd.). Departmental Lecture Theatre, The University, **Leeds.** 3.30 p.m.

MANCHESTER JUNIOR BRANCH. *Synthetic Fibres in the Hosiery Industry.* Member of the staff of Clayton Dyestuffs Co., Manchester. (To be announced later). College of Technology, **Manchester.** 6.30 p.m.

Friday, 4th March 1955

MIDLANDS SECTION. MIDLANDS SECTION DINNER. Kings Head Hotel, **Loughborough.** 7 p.m.

Wednesday, 9th March 1955

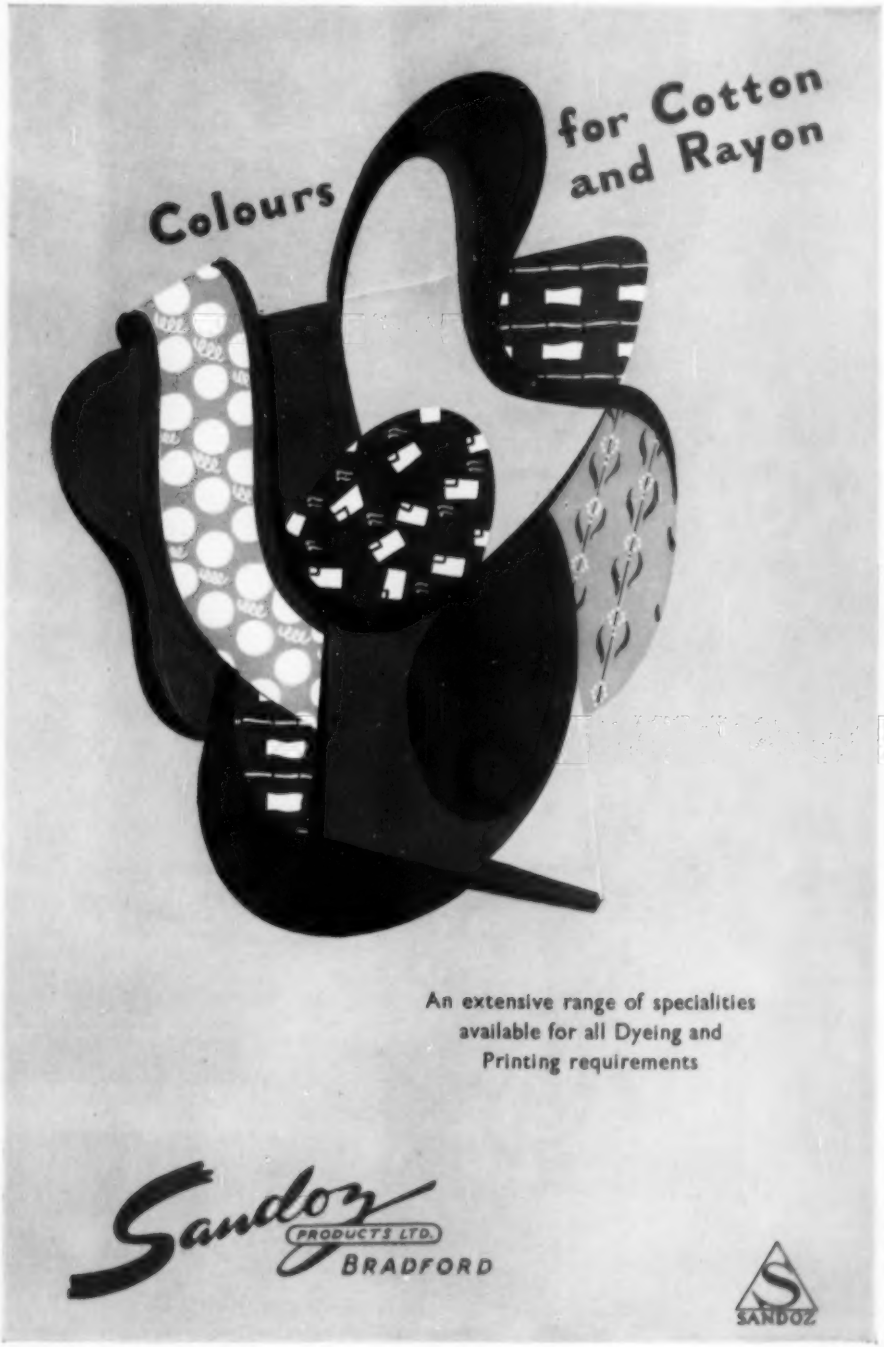
NORTHERN IRELAND SECTION. Film Evening. (Joint Meeting with Textile Institute). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Thursday, 10th March 1955

MIDLANDS SECTION. *The Diffusion of Vat Dyes into Cellulose.* R. H. Peters, Esq., Ph.D., F.S.D.C., and T. Watson, Esq., Ph.D. (Dr. Peters lecturing). Gas Theatre, **Nottingham.** 7 p.m.

WEST RIDING SECTION. Title Later. Dr. F. F. Elsworth (Wool Industries Research Association). The Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

continued on page xxxi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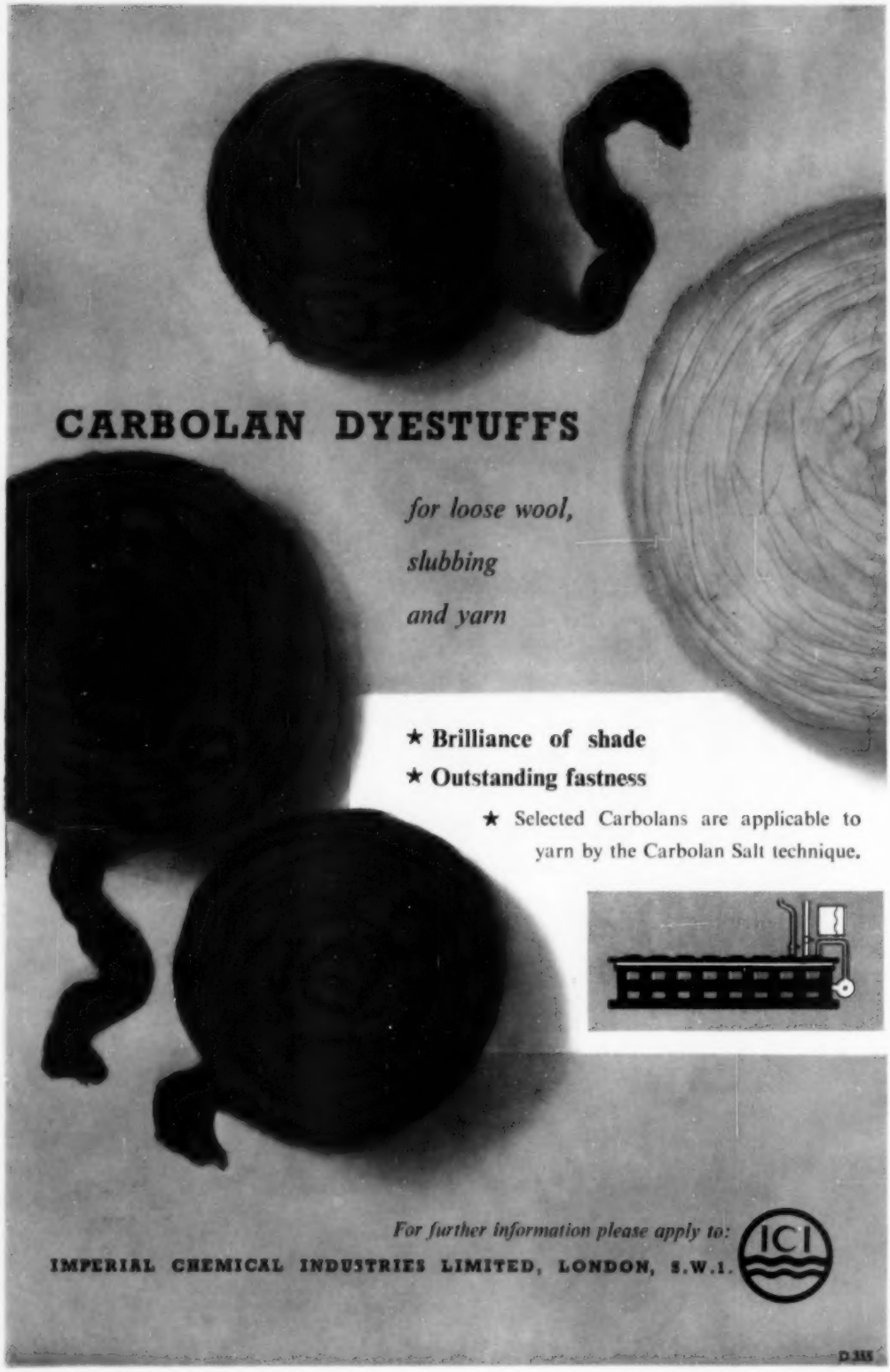
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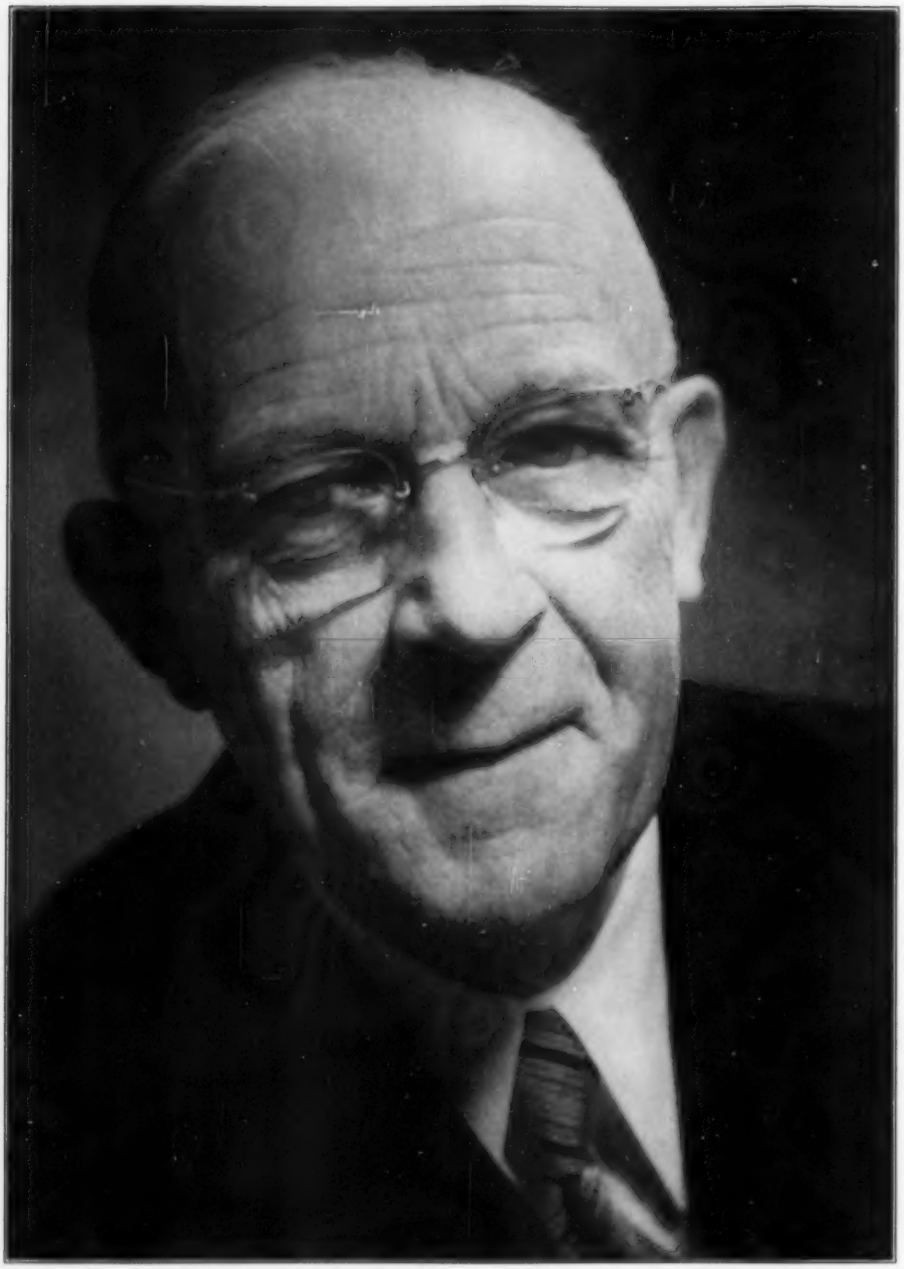


ARTHUR ZITSCHER PH.D.

Perkin Medal for his Work leading to the Discovery of the New Class of Azoic Dyes, based on the Arylamides of o-Hydroxycarboxylic Acids

THE JOURNAL

OF THE

Society of Dyers and Colourists

Volume 70 Number 12 DECEMBER 1954 *Issued Monthly*

Proceedings of the Society

Presentation of the Perkin Medal to Dr. Arthur Zitscher

Meeting held in the Large Chemistry Lecture Theatre, the University, Manchester, on 15th October 1954, Mr. G. S. J. White in the chair

Mr. G. S. J. WHITE (*Chairman of the Manchester Section*) extended a warm welcome to Dr. Zitscher and to his colleagues— Dr. W. Neumann, Dr. A. Sieglitz, and Dr. E. Thiel— who had accompanied him from Frankfurt-am-Main.

Mr. WHITE said: It is indeed pleasant for me, both personally and as the Chairman of the Manchester Section of the Society of Dyers and Colourists, to have the honour of introducing our guest, Dr. Zitscher, to you. In his discourse he will tell you the details of his association with the discovery of the textile-colouring properties, and the uses in pigments, of the arylides of 2:3-hydroxynaphthoic acid and related compounds.

For my part, I would like to stress how appropriate it is that our ceremony tonight takes place here in Manchester of all cities. Were we to cast our minds back to the time of the initial discovery, we would recall how Lancashire's textile industry still bestrode the world, a cotton colossus, and equally dominating in its own sphere was the German organic chemical industry. There is no doubt that some of their great strength was built together. The new inventions of the organic chemist were first rushed to dark mills in our misty valleys for practical evaluation and development before being proclaimed as discoveries of outstanding technological importance to the world in general.

Among those who had some part in this work was Mr. F. Scholefield, a Past President of the Society, whom we welcome here tonight. His work on dyeing, that of Mr. C. Blower of the Calico Printers' Association Ltd. on textile printing, and that of other chemists and colourists, some now no longer with us, consolidated the views of the inventors of the "Naphtol" dyes and, after the 1914–1918 War, led to their widespread employment in dyehouses and print shops both here and over many seas.

Our British dyemaking industry has many roots in Manchester. Before World War II it was associated in a joint venture established here to exploit and develop the Zitscher products. Now, at this moment, it is certain that some part of the present activity of chemical plant only a very few miles to the East, North, and West of this place is concerned with the manufacture of arylides and their associated bases.

But this is not the whole story, for we can also be proud of the contribution made by Manchester academic workers to the knowledge and understanding of these products. We do not forget the original work by the late Professor F. M. Rowe, by Professor W. Bradley, and by Dr. A. Burawoy at the College of Technology. Neither must we omit to note the powerful association of this building, the Perkin Laboratory, and those who follow the lead given by the work in this university of W. H. Perkin, Jr., in the whole field of the chemistry of dyes.

The Perkin Medal is awarded by the Society of Dyers and Colourists to commemorate the founder of the synthetic dye industry and "for discoveries or work of outstanding importance in connection with the tinctorial arts". Previous recipients associated with dyemaking have been Graebe and Liebermann, Adolf von Baeyer, A. G. Green, Vidal, Prud'homme, Schmidt, and Baddiley.

I have endeavoured very briefly to indicate the stimulus which has been given to industry, commerce, technology, and science by the outstanding discoveries of Dr. Zitscher and his colleagues, and I have great pleasure in presenting him to you as being in the true tradition, an illustrious and proper candidate for the award of the Perkin Medal.

Mr. FRED SMITH (*President of the Society*) said: I am very proud to be the one to present to you the Society's most coveted medal in honour of

your discovery, a discovery that has helped to beautify the world with fast colours. Your invention has been of such importance that today American, British, and Continental dyemakers together are unable to satisfy the world demand for dyes of this type, which has been increased by their applicability to the newer man-made fibres.

It is therefore only just that you should be the recipient of our highest award, which I now present to you as the surviving member of the Laska–Zitscher partnership. I trust that you will live many years to treasure this gold medal, which you take back with you to Germany as a testimony of British recognition of your valued services to the world-wide community, and that you will retain happy memories of this day.

Mr. SMITH then presented to Dr. ARTHUR ZITSCHER the Perkin Medal bearing the citation—

> *For his work leading to the discovery of the new class of azoic dyes, based on the arylamides of o-hydroxycarboxylic acids.*

Dr. ARTHUR ZITSCHER said: I am deeply conscious of the honour bestowed on me by the Society of Dyers and Colourists in the award of the famous medal which bears the image of Sir William Henry Perkin, who provided the first impulse to the synthetic dye industry. I thank you, Mr. President, and through you the members of the Council and members of the Society with all my heart for the high distinction which you have conferred upon me by giving me this medal.

I was deeply moved when the President of your Society took part in the inauguration of the new laboratory at the Offenbach works which has been named after my colleague Laska and myself. This kind gesture combined with the award to me of the Perkin Medal has formed a personal tie between us, which I am sure will last for life.

It is a matter for deep satisfaction that you have granted this distinction to me, a foreigner, a fine example of the international solidarity of scientific workers, who are concerned only with merit and not with nationality. I would never have dared to hope for such an honour and, as you can well imagine, I am very happy and proud of it. In a way this day is the crowning event of my life.

But it is not my merit alone which brings me the highest award your Society can bestow. I am the only survivor of a *team* of chemists which started the original work on Naphtol AS. In the first place I want to mention my late colleague, AUGUST LEOPOLD LASKA, who played a fundamental part in broadening and developing this new class of dyes. A great number of able chemists and colourists have furthermore helped in the sometimes arduous laboratory work and in the application of the new components under practical conditions. All these men deserve recognition and praise.

Mr. President, I wish to thank you again for the outstanding distinction conferred on me by your Society.

Dr. ZITSCHER then read an abridged version of the following paper.

The Development of Naphtol AS Dyes

ARTHUR ZITSCHER

The history and the development of azoic dyes based on the arylamides of *o*-hydroxycarboxylic acids are reviewed. The relation between the chemical constitution of an azoic dye and its substantivity on cellulose is discussed, and the paper concludes with an account of stabilised diazo components.

When, in 1859, Peter Griess discovered the diazo reaction and thus the azo dyes, the way was opened for the manufacture of dyes for colouring animal fibres. Dyeing of cotton was, however, still restricted to the application of vat dyes (indigo) or mordant dyes (alizarin). It was not until 1879 that Griess prepared a dye—

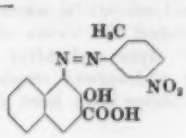
Benzidinedisulphonic acid → β-Naphthylamine
Benzidinedisulphonic acid → β-Naphthylamine

having affinity for cotton, but this had no technical importance. The first dye for cotton which could be used in practice was Congo Red, first made by Boettiger in 1884.

In 1880 the brothers Holliday, and independently of them Grässler, had suggested producing insoluble dyes on cotton by impregnating the fibre with sodium β-naphtholate, and then treating it with diazotised β-naphthylamine or xylidine, a process which remained of interest even after the discovery of the substantive cotton dyes, since the latter had only poor wet-fastness properties. It was only in 1889 that this process was brought to technical perfection by the studies of Koechlin, von Gallois, and Ullrich[1]. It was now suggested that diazotised *p*-nitroaniline should be combined with β-naphthol, and the resulting dye, Para Red, has become an important product of the so-called "ice colour industry", on account of its good fastness to washing and to light and its simple mode of application in textile printing. But for dyeing yarns and the like this process was not successful, since it was not possible to overcome the difficulty of drying the yarns impregnated with sodium β-naphtholate in such a manner that uniform dyeings could be obtained.

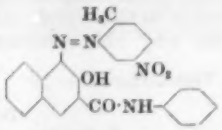
This was the state of the art in 1910, when the Offenbach plant—at that time belonging to the Chemische Fabrik Griesheim-Elektron, now to the Farbwerke Hoechst AG.—started to work in a direction which was to bring the "ice colour industry" to a new peak.

While setting up a range of lake colours, the Research Laboratory of the Offenbach Works received a complaint about the pigment from diazotised 2-amino-4-nitrotoluene and 2:3-hydroxynaphthoic acid—



a beautiful bluish-red pigment of better fastness to light than Lithol Red. Experiments on a practical scale, however, had shown that the colour of this dye changes to brown when it is ground with boiled linseed oil in the presence of a large amount of aluminium hydroxide, such as is customarily used in preparing printing inks, so that it could not be used in practice. The same behaviour is shown by dyes of a similar constitution prepared from 2:3-hydroxynaphthoic acid, which points to a characteristic property of combinations of this structure. This deficiency could not be removed by repeated variation of the methods for producing the lakes. The reaction was thoroughly investigated, and it was realised that the brown products were complex compounds formed in the presence of linoleic acid and that the carboxyl group is not capable of forming colour lakes in the presence of a large amount of aluminium hydroxide. Attempts were therefore made to avoid the detrimental effect of the free carboxyl group by blocking it. There came into consideration mainly functional derivatives of 2:3-hydroxynaphthoic acid, such as esters and arylides. The esters were at once dismissed from consideration, since such lakes could hardly be expected to exhibit the necessary fastness to oil.

The first pigment dye from the anilide of 2:3-hydroxynaphthoic acid, with diazotised 2-amino-4-nitrotoluene—

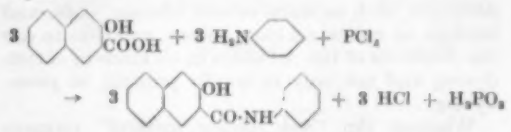


was produced in the laboratory on 6th December 1910. It was a complete success. We obtained a brilliant red pigment which was fast to oil and light and did not change in hue in the preparation of the printing ink.

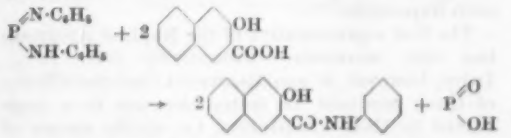
We now started to study this new class of pigment dyes on a large scale, and in the course of the following years we were able to set up a range of valuable pigment dyes, which were first marketed under the name of *Grela* dyes. Today they are on the market under the name of *Permanent* dyes. These products have good tinctorial power and very pure hues, and they are distinguished by their good fastness to light. On account of their excellent properties, these representatives of the group of Permanent dyes have found extensive application in the printing ink, paint, and varnish industries.

The anilide of 2:3-hydroxynaphthoic acid was not a new substance: it had been described by Schöpff in 1892 [2]. But the process described by Schöpff was not feasible for manufacturing the product on a large scale, as the yield was only moderate. We were lucky in finding a technically simple modification which now enables us to produce all arylides, even those from negatively substituted bases, in a smooth reaction on an industrial scale and in good purity and very high yield.

This process does not proceed according to the equation—



but probably phosphazobenzene anilide $C_6H_5{\cdot}N{:}P{\cdot}NH{\cdot}C_6H_5$ is first formed from phosphorus trichloride and aniline. This compound then reacts with 2:3-hydroxynaphthoic acid to form the anilide—



At that time there was discussion in the textile periodicals on a problem which was said to be important, namely the application of the ice colour method to the production of indigo shades fast to light and washing. In this connection the combination of dianisidine and 2:3-hydroxynaphthoic acid, known since 1891, was also mentioned, as this product in calico printing, even without the addition of copper, yields a blue, but this is not fast to acids. The carboxyl group seems to interfere as in the case of the lakes. Corresponding experiments in textile printing in which the anilide of 2:3-hydroxynaphthoic acid was used instead of β-naphthol as ground component gave the expected results: the blue obtained was fast to acids. We were now in a position to produce an indigo-blue ground which, in addition to possessing good fastness to light, was fast to washing and acids, resistible, and even dischargeable. Thus it was possible to produce the very popular blue–white–red style.

This result induced our Colouristic Department to study the application of the anilide as a substitute for β-naphthol in the production of ice colours. This so far had been of no major interest because the price was considered unfavourable. The anilide of 2:3-hydroxynaphthoic acid (Naphtol AS) was put on the market, the first representative of a new class of ice colour components. The first circular letter issued to customers, in August 1912, illustrates only the application of Naphtol AS to piece goods and in textile printing. The bases are indicated by their chemical names, and the colours obtained are shown opposite those produced on β-naphthol ground. It goes without saying that these dyeings were produced *with intermediate drying* of the impregnated material, in strict imitation of the old ice colours.

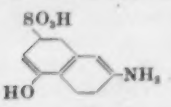
At the end of 1912 we made a discovery which decided the direction of further development of the Naphtol AS class. We realised that a material impregnated with the sodium salt of Naphtol AS could be developed even *without intermediate drying*: no bleeding as in the case of β-naphthol was noticed. This led to the discovery that the arylides of 2:3-hydroxynaphthoic acid, contrary to β-naphthol, have pronounced substantive properties.

Thus, a method was found of producing fast dyeings by the ice colour method also on wound packages, such as warp beams, cheeses, cops, and rovings, as well as on loose cotton, and thus to use the Naphtols of the AS series in all kinds of cotton dyeing and not only in textile printing or piece-dyeing.

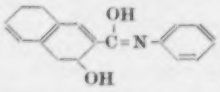
Whereas the "wet dyeing method" requires coupling components of high substantivity so that the dyeings may have good fastness to rubbing, products of lower affinity are preferred in textile printing in order that stripping of the uncoupled residues in the ground is not rendered difficult or even impossible.

The first representative of the Naphtol AS group has only moderate substantivity (viz. 12%). Later, however, it was discovered that the affinity of these products for cotton depends to a large extent on their constitution, i.e. on the nature of the central nucleus and the substituents in the arylide radical, and that by varying these factors it is possible to increase the substantivity to 80–90%, the substantivity of a direct cotton dye of very good affinity.

It is noteworthy that the conjugated double bonds of Naphtol AS have the same arrangement as those of J acid—



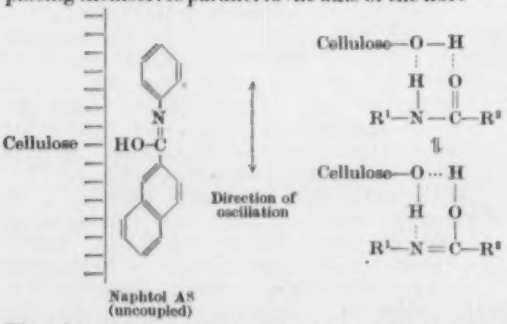
J Acid



Naphtol AS

which itself has some affinity for cotton. Unlike J acid, Naphtol AS is not suitable for building up substantive direct dyes analogous to the known J acid dyes, since coupling modifies the resonance system of the molecules. The axis of oscillation is no longer in the longitudinal direction of the molecule but perpendicular to it. Thus, the substantivity is to a large extent abolished.

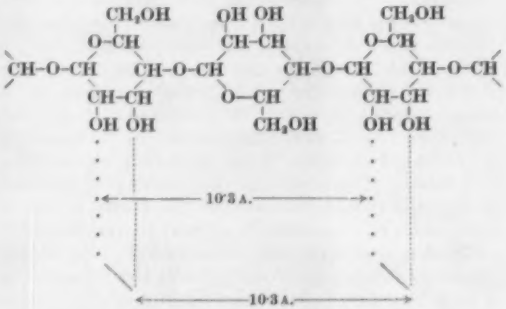
The true nature of the substantivity is not yet clear, but it may be assumed that the dye is attached to the fibre by means of hydrogen bonds, the dye molecules placing themselves parallel to the axis of the fibre [3]—



Naphtol AS (uncoupled)

The adsorption mechanism for substantive Naphtol AS products is, therefore, quite analogous to that of direct dyes.

For good affinity it seems also to be important that the groups capable of forming hydrogen bonds are present as far as possible at intervals of 10·3 A. or multiples thereof, corresponding to the periodicity of cellobiose units forming the cellulose chain [4]—

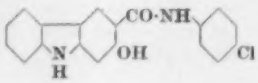
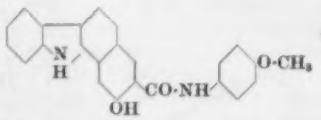


Planar Section of Cellulose Chain

A comparison of Naphtols AS–LB and AS–SG may serve as example (Table I) [4].

Schirm's substantivity theory of conjugated double bonds [5] merely describes a structural arrangement with which experience has usually shown functional substantivity to be associated. It does not explain, however, why arylides of similar structure and containing the same number of conjugated double bonds sometimes show considerable differences in their affinity, depending, for example, on the substituents in the arylide radical. Neither does it explain why the substantivity of the

TABLE I [4]

Naphtol	Formula	Exhaustion (%)	Intramolecular Distance between N and –CO·N (A.)
AS–LB		22–28	7·3
AS–SG		62–70	10·0

α-naphthylamide of 2:3-hydroxynaphthoic acid (Naphtol AS–BO) is 25%, whereas that of the β-naphthylamide (Naphtol AS–SW) is 45%. Spiegler [4] has shown by means of molecular models that the differences in affinity are probably due to the fact that the products conform to different extents to the favourable conditions postulated by Vickerstaff [6]—

(1) The molecules should be capable of adopting a linear configuration.

(2) The aromatic nuclei should be able to arrange themselves in a coplanar position to each other— the presence of a system of conjugated double bonds promotes the coplanarity of the molecules by resonance and probably favours the formation of hydrogen bonds at the end of the conjugated system [7].

TABLE II [3–5, 7]

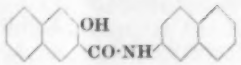
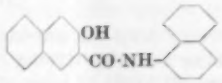
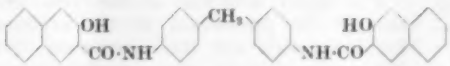
Naphtol	Formula	Model (Fig.)	Shape of Molecule	Substantivity (%)
AS-SW		1	Linear	45
AS-BO		2	Angular	25
—		3	(Top view) Angular	24
		4	(Side view) Non-coplanar	
—		5	Linear	70

FIG. 1–5—SPIEGLER'S MOLECULAR MODELS* (cf. Table II)

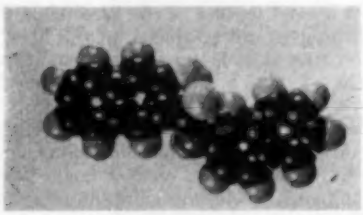


FIG. 1 — Naphtol AS-SW

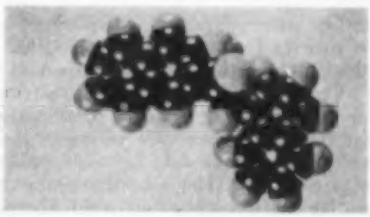


FIG. 2 — Naphtol AS-BO

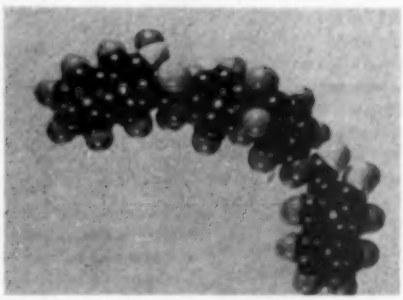


FIG. 3— Top View

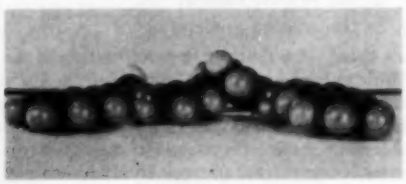


FIG. 4 — Side View

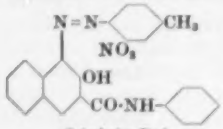
FIG. 5

*Reproduced from the *Journal of Organic Chemistry*[4] by permission.

(3) The molecules should contain groups which are capable of forming hydrogen bonds.

Examples of Spiegler's molecular models show apparently that it is possible to explain, on the basis of the above theories, the differences in substantivity between Naphtol AS products of the same fundamental structure (cf. Table II and Fig. 1–5).

To return to the history of the development of Naphtol AS dyes, the standard red of the new class of ice colours was formed by combination of diazotised *m*-nitro-*p*-toluidine with Naphtol AS—



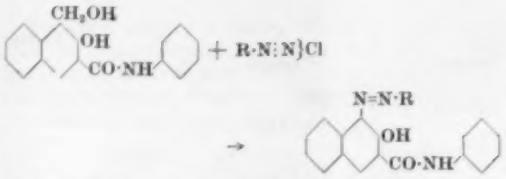
Griesheim Red

a dye of special value, possessing such good fastness properties that it could displace Para Red to a great extent and even rival Turkey Red.

According to private information, another German firm had already investigated the use of 2:3-hydroxynaphthanilide as a component for ice colours. The Colouristic Department of that firm, however, had merely printed the combination with *p*-nitroaniline, which was the ordinary method of testing new azo components in this field, and had decided on complete rejection. They were right in doing so, for this dye possesses no advantages with regard to colour and fastness properties as compared with Para Red. Perhaps the same would have happened to us if the quality of other red combinations had not been already known to us from our work with pigments.

Our enthusiasm was considerably dampened after a short time, and use of the new dyes for dyeing yarns was seriously endangered, when it was found that the ground was sensitive to air. Impregnated hanks which had been exposed to air for a long time, especially those which had been hydroextracted, led to streaky dyeings. This partial alteration of the impregnated hanks is caused by hydrolytic decomposition of the sodium salts of the arylides. According to Löwenfeld [8] this is due to the fact that coupling components of the Naphtol AS series are present in the impregnating bath not only as disodium salts but partly as monosodium salts.

This drawback could be completely overcome by adding formaldehyde to the alkaline impregnating bath. It was not until twenty-five years later that the constitution of the resulting compounds was definitely established by Neber and Kubitzky [9]. 1-Hydroxymethyl compounds of the Naphtol AS products are formed, the alkali-metal salts of which are not so readily hydrolysed as those of arylides of 2:3-hydroxynaphthoic acid. During the coupling process the hydroxymethyl group is completely split off, and the same dyes are obtained as with the Naphtol AS products themselves [9]—



This was the important step for introducing the Naphtol AS products for the dyeing of yarn, winding bobbins, and all kinds of loose material.

The rapid solution of the two problems—namely the production of the arylides on an industrial scale and the overcoming of the difficulties of application by means of the formaldehyde process—has been of decisive importance for the introduction and the development of the Naphtol AS dyes.

A second product, Naphtol AS–BS, appeared on the market as early as 1912. In general, it yielded more bluish and clearer colours than its elder brother, Naphtol AS.

The first pattern card for dyeing yarn on the basis of Naphtols AS and AS–BS was issued in 1914.

It is a special feature of the azoic class that the dyes themselves are produced on the fibre by the colourist, who thus has a special responsibility in this field. I feel it is my duty to recall with gratitude the co-operation of the staff of the Colouristic Department of our plant. Although the chemical method is in principle quite simple, its colouristic development, until it could be applied on a commercial scale, was slow and laborious, and the main share in this development has been contributed by the Colouristic Department. Exemplary co-operation, daily contact, and even personal friendship between the men in the laboratory and those in the Colouristic Department helped to overcome the difficulties and to develop new methods which guaranteed safe working in practice. I wish to mention Herr F. Kunert, Herr E. Acker and Dr. J. Rath, Dr. W. Christ and Herr K. Jellinek, who rendered great services in the Colouristic Department in Offenbach before it was transferred to Leverkusen.

The First World War severely hindered the utilisation of the discovery: only after 1920 did further development take place.

Although the chemical method itself is very simple, it may be varied in many ways. The possible combinations may be varied in three different ways—

(1) In the diazo radical

(2) In the arylide radical

(3) In the central nucleus,

in the third case either by substituting in the naphthalene radical or by replacing it by other aromatic nuclei. It is, of course, out of the question to attempt the preparation of all possible variants, but the mere task of systematic research on this basis was too great for our relatively small plant at Offenbach. The laboratories of other plants were therefore included in the research. This co-operation has been extremely profitable and has contributed a great deal to raising the Naphtol AS

class to the present-day high standard. The co-operation within the Naphtol AS committee which was founded after the merger of these firms into the former I.G. Farbenindustrie AG has proved of particular advantage, as the knowledge and the experience of each individual plant could be utilised in an ideal team-work. I regret that I cannot mention the names of all those who contributed to the further development of the Naphtol AS class, their number being far too large. It may give some idea of the work done that, during the eight years 1930–1938, 4022 new coupling components and 5905 new bases, viz. 9927 separate compounds, were tested, out of which only 13 new coupling components and 33 new diazo components, viz. 0·46%, were accepted.

The success of all this work, apart from the range of yellow dyes, has always been based on the principle of the original discovery, the use of arylamides of *o*-hydroxyarylcarboxylic acids, which could not be replaced hitherto by another principle, at least not without a decrease in fastness properties.

Shortly after the First World War we succeeded also in closing a serious gap in the range of azoic dyes. Until then the production of pure yellows had been impossible by this method. It was now found that the inclusion of substantivating groups in arylamides of acylacetic acids imparts to them affinity for the cotton fibre, so that they can be used as grounding components like the other Naphtols of the AS series (Naphtol AS–G). The resulting greenish-yellow to reddish-yellow shades are very clear and, in combination with suitable bases, absolutely fast to kier-boiling; they are not, however, dischargeable, and they possess only medium fastness to light. The substantivity and the fastness to light can be considerably improved by the use of arylides of terephthaloylbisacetic acid as diazo components. 2-Acylacetamides of the benzothiazole series also yield dyeings of very good fastness to light which are also dischargeable. Recently, suggestions in this field from laboratories in other countries have become known, but these are merely variations of the same basic principle.

The post-war years brought the first fast bordeaux combinations — Naphtol AS–BO (*α*-naphthylamide) with Fast Red B Base (2-amino-5-nitroanisole) and Naphtol AS–RL (*p*-anisidide) with Fast Red RL Base (5-nitro-2-aminotoluene), the latter yielding a red surpassing in light fastness any dye known before.

In 1923 Naphtol AS–SW (*β*-naphthylamide) was put on the market. It was the first coupling component which had a pronounced affinity for the cotton fibre: its substantivity is 45%, and with the addition of salt 60%. This product has such great affinity that impregnated goods can be rinsed with salt solution without diminishing the depth of dyeing. This is of particular importance for producing dyeings having good fastness to rubbing. The combination of Naphtol AS–SW with bases substituted in positions 2 and 5 relative to the amino group has proved to be of special value if at least one of these substituents is a halogen atom or either $-SO_2 \cdot X$ or $-CO \cdot X$*. With regard to the substituents $-SO_2 \cdot X$ or $-CO \cdot X$, the combinations with other Naphtols of the AS series also yield good results. On this basis dyeings of very good fastness to bleaching and good fastness to boiling with caustic soda could be produced. The combination of diazotised 2-amino-4-chlorotoluene (Fast Red KB) with Naphtol AS–SW yields a clear red and is up to the present day one of the most valuable combinations.

It is worth mentioning that Naphtol AS–SW combined with Fast Black LB Base gave the first fast black in the Naphtol AS series.

Our further work was concentrated on three problems—

(1) Production of coupling components of high substantivity

(2) Discovery of combinations of good fastness to caustic-soda boiling

(3) Production of coupling components with increased fastness to light.

Naturally, in the course of these investigations combinations were found which possessed both good light fastness and substantivity or fastness to caustic boiling.

1-(2:3-Hydroxynaphthamido)-2:5-dimethoxy-4-chlorobenzene (Naphtol AS–LC) shows a high affinity and generally yields dyeings of high fastness to light. Further development resulted in Naphtol AS–S, 2-(2:3-hydroxynaphthamido)-3-methoxydiphenylene oxide, the most substantive Naphtol for reds, which is absorbed by the fibre to 80% exhaustion in the absence of salt and to 95%, i.e. practically quantitatively, when salt is added. Correspondingly, the dyeings possess excellent fastness to rubbing.

The combination of diazotised 2-amino-5-chlorotoluene (Fast Red TR) with 2-(2:3-hydroxynaphthamido)-5-chlorotoluene (Naphtol AS–TR) was recognised as a dye of very good fastness to boiling with caustic soda. This combination yields a shade very similar to that of Turkey Red and has found extensive application.

The fastness to light of the Naphtol AS dyes could be favourably influenced by including alkoxy groups in the arylide radical. A representative of this group is Naphtol AS–RL, and another representative is Naphtol AS–OL, the *o*-anisidide, whose combination with diazotised 2:5-dichloroaniline (Fast Scarlet GG) should be mentioned on account of its brilliant colour and its high fastness to light.

Apart from Naphtol AS–LC, Naphtol AS–LT, 1-(2:3-hydroxynaphthamido)-4-methoxy-2-methylbenzene, and Naphtol AS–ITR, 1-(2:3-hydroxynaphthamido)-2:4-dimethoxy-5-chlorobenzene, can also be used with advantage as grounding components whose combinations generally possess increased fastness to light.

To this category belongs also the best dye of the group of red dyes, the combination of Fast Red ITR (1-amino-2-methoxybenzene-5-sulphodiethylamide) with Naphtol AS–ITR, which in shade and

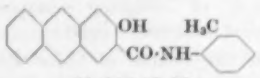
*X = Alk, Ar, Aralkyl, NH·Alk, NH·Ar, or NH·Aralkyl.

fastness to light is very similar to Turkey Red and can be dyed more cheaply than the latter. It has, therefore, entered successfully into competition with Turkey Red.

Two other products of the AS series—Naphtol AS–BG, 1-(2:3-hydroxynaphthamido)-2:5-dimethoxybenzene, and Naphtol AS–BR, bis-2:3-hydroxynaphthoyldianisidine—made it possible for the first time to obtain reddish browns.

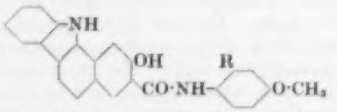
Definite browns could be obtained by the combinations with Naphtol AS–LB, 2-hydroxycarbazole-3-carboxy-*p*-chloroanilide, and Naphtol AS–DB, 1-(3-hydroxydiphenylene oxide-2-carbamoyl)-2:5-dimethoxybenzene, the latter of which yields deep browns.

The addition of further ring systems to 2:3-hydroxynaphthoic acid led to further valuable arylides, viz. Naphtol AS–GR, 2-hydroxyanthracene-3-carboxy-*o*-toluidide—



Naphtol AS–GR

which in combination with blue bases yields bluish greens, and the two black components, Naphtols AS–SG and AS–SR—

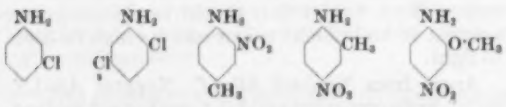


Naphtol AS–SG (R = H) and Naphtol AS–SR (R = CH_3)

which, together with certain bases, e.g. Fast Red B, yield blacks of very good fastness to light. Both products have a high substantivity, viz. 95% without the addition of salt.

The first bases used as diazo components for Naphtol AS were those corresponding to the diazo components generally used for coupling with β-naphthol. When the yarn-dyeing process was introduced, a new range of bases could be recommended as "Fast Bases" on the basis of the experience gained in the meantime. I wish to mention some of these simple representatives which are still today important intermediate products, e.g.—

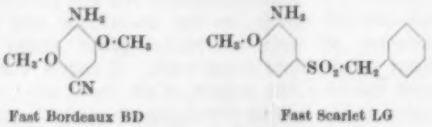
FAST BASES



Orange G Scarlet GG Red GL Red RL Red B

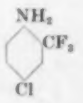
Furthermore, chlorotoluidines and chloroanisidines were used, such as Fast Reds KB, TR, and R (2-amino-4-chloroanisole). Aminodiphenyl ethers substituted by chlorine also proved to be valuable components for reds (Fast Red FR = 2-amino-4:4′-bischlorophenyl ether or Fast Red FG = 2-amino-4-chlorodiphenyl ether).

Recognition of the favourable influence of negative substituents upon the fastness to light led to the manufacture of further bases with, for instance, NO_2, CN, $SO_2{\cdot}X$, and CO·X* groups, such as—



Fast Bordeaux BD Fast Scarlet LG

The effect of the trifluoromethyl group as a substituent is of particular interest, since this group is strongly negative like the nitro group, but has no bathochromic effect as has the latter. Bases substituted by the trifluoromethyl group in the *meta* position shift the colour markedly toward the yellow, e.g. Orange GGD, 1-amino-2:3-bistrifluoromethylbenzene. Combinations of these bases with arylides of 2:3-hydroxynaphthoic acid are suitable for bringing about the transition from the orange to the orange–yellow dyeings produced by means of Yellow Naphtols. Dyeings produced with Fast Scarlet VD—

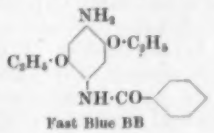


Fast Scarlet VD

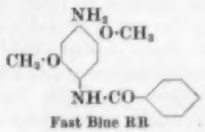
on Naphtol AS yield clear scarlets of high fastness to light and to weathering.

Garnet shades can be obtained with *o*- and *m*-aminoazotoluenes, the commercial Fast Garnet Bases.

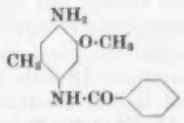
A new group of bases, derivatives of monoacylated *p*-phenylenediamines substituted in positions 2 and 5, supply more or less blue shades, depending on the kind of substitution—



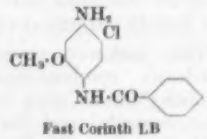
Fast Blue BB



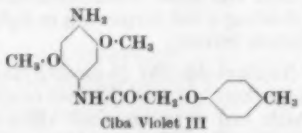
Fast Blue RR



Fast Violet B

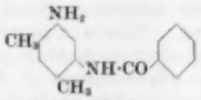


Fast Corinth LB



Ciba Violet III

The red combination from a base of analogous structure—



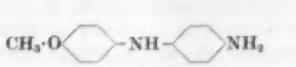
Fast Red RBE

* See footnote on p. 535.

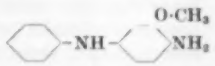
and Naphtol AS–SW is distinguished by its very good fastness to boiling with caustic soda.

In the field of blue dyes there must also be mentioned the Variamine Blue brands, which are marketed only in the form of dyeing salts. They also are derivatives of *p*-phenylenediamine, of the formula—

In addition to this product, called in the form of the dyeing salt *Variamine Blue Salt RT*, the dyeing salts of the following bases are marketed—



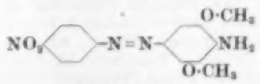
Variamine Blue B



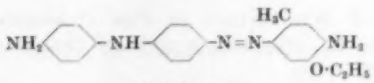
Variamine Blue FG

On account of their low coupling energy they are used mainly in textile printing for the production of white and coloured effects on a fast blue ground by means of aluminium sulphate resists. Thus, the blue print became a domain of the Variamine Blue resist style, which displaced to a large extent indigo discharge printing and vat blue printing.

For the production of blacks 4:4′-diaminodiphenylamine (Fast Black B) was used, and later, with simultaneous improvement of the fastness properties, aminoazo compounds, such as—



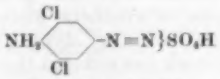
Fast Black K



Fast Black G

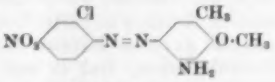
in the form of their dyeing salts.

Diazo components producing browns on Naphtols normally giving reds included Fast Brown Salt RR—



Fast Brown Salt RR

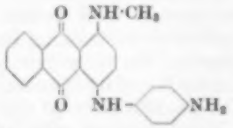
which in combination with Naphtol AS–OL yields a dischargeable reddish-brown dyeing, and Fast Brown Salt V—



Fast Brown Salt V

a derivative of *o*-aminoazobenzene.

Several suggestions have also been made for the production of greens with corresponding bases. The basic principle consists in diazotising a blue dye containing an amino group and coupling the diazo compound with a Yellow Naphtol. These combinations, however, had no technical success. A product of this type was on the market for a short time under the name *Duratol Green G* (ICI)—

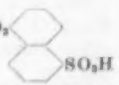


Recently, it has been suggested that for this purpose phthalocyanines substituted by amino groups might be used.

It is an essential feature of azoic dyes that the dye itself is not produced by a manufacturer and merely applied to the fibre by a dyer or a printer as is the case with other groups of dyes. In this case the dye is produced by the dyer himself, who is supplied with the two primary products—diazo component and coupling component—and from them produces the dye on the fibre. This involves, of course, the necessity of diazotising the bases, which may easily lead to failures, particularly in the case of bases containing strongly negative groups as substituents. In countries whose technical institutions are rather primitive, e.g. some countries of the Far East, there was no possibility of suitably carrying out the diazotisation. Thus, the necessity arose of producing stable diazo salts which could be handled without any risk. The solution of this problem on an industrial scale deserves special appreciation. A series of such stable diazo salts was already known, but in practice they had no success on account of their relative instability. Fast Colour Salts of this type are listed in Table III.

TABLE III

Stabilised Diazo Components ("Fast Colour Salts")

Diazonium chloride–zinc chloride double salts ... ... (Also double salts with $MnCl_2$, $CoCl_2$ and $CdCl_2$)	$R{\cdot}N{:}N\}Cl,\frac{1}{2}ZnCl_2$
Diazonium acid sulphates	$R{\cdot}N{:}N\}SO_4H$
Diazonium alkyl sulphates	$R{\cdot}N{:}N\}SO_2{\cdot}O{\cdot}Alk$
Diazonium chlorides	$R{\cdot}N{:}N\}Cl$
Diazonium fluoroborates	$R{\cdot}N{:}N\}BF_4$
Diazonium benzenesulphonates ... (Also with NO_2, Cl, and $NH{\cdot}CO{\cdot}CH_3$ as substituents)	$R{\cdot}N{:}N\}SO_3{\cdot}C_6H_5$
Diazonium acid 1:5-naphthalenedisulphonates	

In accordance with the requirement of the printing industry for dye preparations allowing goods to be printed without a preliminary impregnation, early suggestions were made to use mixtures of β-naphthol with diazo preparations which do not couple in the alkaline printing paste, but effect development of the dye on acid after-treatment. *anti*-Diazoates, all of which were prepared in practice from *p*-nitroaniline, were used as latent diazo compounds for the manufacture of *Nitrosamine Red*. These preparations based on β-naphthol were not, however, successful in the printing industry. The same principle, but applied to Naphtol AS products,

led to the development of the Rapid Fast dyes, whose range of colour extends from yellow to blue.

As the nitrosamines used contain nitro groups, the stability of the corresponding Rapid Fast dyes is limited, whereas the H brands, prepared from nitrosamines substituted by chlorine, exhibit better stability. The weakest point of this series was the blue, which was prepared with the aid of the nitrosamine from dianisidine; blacks could not be produced at all.

For the production of blues and blacks the Rapid Fast range could be supplemented by the Rapidazol dyes. They are mixtures of diazosulphonic acids of the *p*-aminodiphenylamine series with Naphtols of the AS series, which can be developed by ordinary steaming.

Another group based on the principle of Rapid dyes is marketed under the trade name of Rapidogen dyes. These printing preparations contain the diazo compounds in the form of diazoamino compounds stabilised with primary or secondary amines containing water-solubilising groups. Depending on the structure of the Rapidogen used, the print is developed by the action of acid or neutral steam. An important factor in the usefulness of such Rapidogen dyes in practice is the adjustment of the diazo compound to a stabiliser which forms a diazoamino compound which can be easily split off under the conditions of the developing process. The Rapidogen dyes have the advantage over the Rapid Fast dyes that diazoamino compounds can also be obtained with bases from which no *anti*-diazoates can be obtained. Thus, the Rapidogen dyes cover a wider range of colours with a diversity of shades, including green and black, than the Rapid Fast dyes.

The tendency to transfer the production of the dyes again to the manufacturer, in order to release the application department and simultaneously utilise the good properties of the azoic dyes, has led to the suggestion of converting such pigment dyes by means of suitable reagents into a reversible form which is soluble in water. After the dyeing process the solubilising groups are split off again, and in this manner the dye is fixed on the fibre in an insoluble form. Products of this kind have been marketed, e.g. the Neocotone (Ciba) dyes.

Although the dyeing of native and regenerated cellulose is the main field of application of the Naphtol AS dyes, they are used also for dyeing other fibres, such as wool, silk, and acetate rayon, but to a smaller extent. For these purposes special processes have been worked out.

The Naphtol AS (azoic) class of dyes, discovered more than forty years ago, has steadily grown, and now includes a range of shades extending from yellow to black, which, on the average, are distinguished by high fastness properties. Their application, together with vat or Indigosol dyes, enables the colourist to produce by a simple method a special class of beautiful coloured goods with very good fastness to washing and with other good fastness properties.

* * *

I am tempted to call the carboxyarylamide group a "magic key", with the aid of which it has been possible to raise the azoic class of dyes from a low to a surprisingly high level of fastness properties, as your President said in Offenbach:

> *The Naphtol AS dyes filled a gap in the range of fast colours which no other class of dyes could have closed until the present day.*

Although you have now conferred the high honour of your Perkin Medal on me personally, which makes me extremely happy, I have to stress once more that I feel myself to be only the representative of a great group of coworkers and men in practical mill-work, who also have given valuable hints for our own investigations. And, if the practical colourist produces with the tools we give him beautiful creations of art, which delight and adorn our ladies, the saying of the old master Perkin becomes true:

> *The end result of all our work shall be the benefit of mankind.*

(*MS. received 16th October 1954*)

References

[1] Cf. Diserens, *Die, neuesten Fortschritte in der Anwendung der Farbstoffe* (Basle: Verlag Birkhäuser), **1**, 502 (3rd edition 1951).
[2] Schöpff, *Ber. deutsch. chem. Ges.*, **25**, 2744 (1892).
[3] Niese, *Ph.D. Thesis* (Leipzig 1953).
[4] Spiegler, *J. Org. Chem.*, **18**, 1292 (1953).
[5] Schirm, *J. prakt. Chem.*, **144**, 69 (1935).
[6] Vickerstaff, *The Physical Chemistry of Dyeing* (2nd edition 1954. London: Oliver & Boyd), p. 183.
[7] Hodgson and Marsden, *J.S.D.C.*, **60**, 210 (1944).
[8] Löwenfeld, *Melliand Textilber.*, **34**, 324 (1953).
[9] Kubitzky, *Ph.D. Thesis* (Tübingen 1937).

Mr. F. SCHOLEFIELD (*a Past President of the Society*), in proposing a vote of thanks to Dr. Zitscher, said:

You will, I am sure, think it proper that I should first, on behalf of this goodly company, congratulate Dr. Zitscher on the award to him of the Perkin Medal.

It is perhaps paradoxical that one of Perkin's great achievements was the production on a commercial scale of synthetic alizarin, one of the most important of the dyes then available. Dr. Zitscher's work has reduced the use of alizarin to small dimensions, a change already begun with Para Red. The origin of these azoic processes was, of course, the Vacanceine Red of Thomas and Robert Holliday of Huddersfield in 1880. No startling success was achieved until the replacement of β-naphthylamine by *p*-nitroaniline by Meister, Lucius & Brüning in 1889. Yet on Naphtol AS *p*-nitroaniline gave no improvement over the β-naphthol combination, and it was the happy substitution of *m*-nitro-*p*-toluidine which gave Naphtol AS its first start.

In 1912 I was employed by a firm of cop-dyers in this city; we were in one respect possessed with a sense of inferiority because a competitor could dye a fast red (Para Red) successfully on cop, and we could not. Reading in a technical journal of a new method of producing ice colours, I had the idea that the method might be applied to cop-dyeing. This was my introduction to Naphtol AS.

With my assistant, Tom Gorton, I obtained very good dyeings on cops with the help of a water pump.

Later in 1912 I joined another firm, taking with me my interest in these new dyes. Early in 1913 my Governing Director visited Frankfurt and Offenbach, and came home impressed by what he had seen, and still more by what had been done in his own laboratories. As a result, in the spring of 1913 my firm placed a contract for 5 tons of Naphtol AS and Naphtol NA*, the only two then available. This was probably the largest order Griesheim had received so far for dyeing purposes: it was large enough to last us, with the help of further purchases in August 1914, until the end of 1918.

Let me turn, if you will allow me, to another personal experience. Rather more than fifty years ago I was a student under Professor A. G. Green, whose contributions to azoic chemistry were also great, in the new University of Leeds. I remember among my fellow workers Dr. Fred Marsden and F. D. Toyne, later chief chemist of Kelsall & Kemp, and I remember a discussion about prospects of employment and advancement which led to the unanimous conclusion that there was little hope of any further great advance in dye chemistry, because this branch of chemistry had by then been pretty well exhausted. You will remember that since 1903 we have had the rise of the vat dyes—anthraquinone, carbazole, and indigoid—the Indigosols and Soledons, the Fanal colours, the optical whitening agents, the Neolans and the Carbolans and the Irgalans, the fast-to-light direct dyes, the phthalocyanine pigments and dyes, the disperse dyes for acetate rayon, Solanile Black, to name a few apart from the manifold forms of the naphthol–base association obtained by Dr. Zitscher and his colleagues. My reason, however, for recalling that talk of fifty years ago is that the gentleman whom we are honouring this evening was recently honoured at the scene of his own work in his own country when new laboratories bearing his name were formally opened, and on that occasion Dr. Zitscher said:

> I have the hope that out of this laboratory there may again come a great discovery. This is by no means so simple, and I can give no tips. We have worked much in these fields, and know that it will not be easy to find unploughed areas in the province of dye chemistry.

I hope that, in spite of the difficulties on which stress has been laid by Dr. Zitscher, the next fifty years will be as prolific in discovery, invention, and technical achievement as the last: they may well be.

I propose that our best thanks be given to Dr. A. Zitscher for his presence and his address here tonight.

* Now called Naphtol AS-BS.

The Dyeing of Felt

D. HAIGH

Meeting of the Midlands Section held at the Masonic Hall, Nuneaton, on 24th February 1954, Mr. S. R. Meadows in the chair

In Part I it is shown that, under practical dyeing conditions, the quality of hat felt, as represented by tensile strength and density, is affected by time and temperature of dyeing, and degree of agitation in the dyeing machine. Types of dyeing machine are compared, and the superiority of the cone dyeing machine is established, especially at the lower temperatures.

In Part II the quality of wool felt, as judged by tensile strength and density, is shown to be influenced by the stage at which dyeing takes place during the felting sequence, the type of dye used, and the time of dyeing. A series of laboratory experiments, using the Furness milling stocks for felting the wool patterns, indicated that the best results are obtained by dyeing at as early a stage as possible for short times with dyes of the acid milling type. The practical limitations are discussed, and preliminary results from factory trials which confirm these findings are quoted.

I—The Effect of Factory Conditions on Quality

Introduction

The investigation reported in this paper forms part of an extensive study of the dyeing of felt as used in the hatting industry.

Since the discovery of the first synthetic dye by W. H. Perkin in 1856, the use of natural dyestuffs such as logwood, orchil, cudbear, fustic, etc. has gradually been superseded, for the dyeing of felt, by level-dyeing acid dyes. It was necessary to apply the natural dyestuffs by the aid of mordants at a very early stage of the felting process in order to obtain levelness and penetration, and then to shrink the dyed felt to the required size. The use of level-dyeing acid dyes now permits dyeing to take place much later in the processing sequence.

Manufacturers of dyeing machinery have concentrated on finding mechanical methods of application of dyes so that dyeing can take place at even later stages of the felting process, and it is now possible to obtain ready penetration of fur felt which has been completely shrunk.

Whilst these two major developments of the past 50–60 years have combined to give great improvements in the dyeing of felt, a really satisfactory method of dyeing felt is still to be found. In most makes of dyeing machinery, ready penetration of tightly felted wool or fur felt can be obtained only with the very level-dyeing acid dyes, which often have only moderate fastness to water and perspiration in full shades, and in practice it is

often necessary to resort to prolonged dyeing to obtain satisfactory results.

The principal object of this study is to find the most satisfactory methods of dyeing both wool and fur felt. The requirements of a successful dyeing method are—

(i) Preservation of the quality of the felt

(ii) Good fastness properties of the resultant dyeing

(iii) Relatively low cost of the process, while achieving satisfactory fastness and quality.

The order of importance depends on point of view, but it is considered essential that quality and fastness should comply with good minimum requirements capable of being readily specified and assessed.

This preliminary investigation is mainly concerned with the first requirement, and deals with the effect on quality when felt of various types is dyed in the different dyeing machines normally used in the hatting industry. Fundamentally, only two types of dyeing machine are represented—

(*a*) Package-dyeing machines (such as the cone dyeing machine), in which liquor is forced under pressure through the felt, which is maintained stationary.

(*b*) Circulatory machines (such as the Cassé dyeing machine), in which the felt is free to move about in the dye liquor, or is moved around by mechanical means, and distribution of dye throughout the felt is achieved by agitation of the liquor.

Only one of the machines investigated, the cone, comes into the first class, but several types of circulatory machine were used, viz. the F.T.M. Crescent (Freeman, Taylor Machines Ltd.), Obermaier, Hudson rotary-drum, and Cassé dyeing machines.

Description of Dyeing Machinery

Short descriptions and photographs of the cone, Cassé, Crescent, and Hudson rotary-drum machines are given by Bird [1]. A description of the Obermaier machine is given below, and some comments are made on the factors, other than effect on felt quality, which should be considered in assessing the worth of each machine.

THE OBERMAIER DYEING MACHINE

This machine consists of an open rectangular stainless-steel vessel fitted with a perforated stainless-steel partition extending along the bottom and up the front. Behind this partition is situated the propeller, which circulates the dye liquor under or over a baffle plate into the body of the vessel. In the normal machine the liquor is circulated by means of an 8-in. propeller and is heated by an open steam pipe situated horizontally under the false bottom. More powerful liquor circulation and even ebullition are given by an improved model with a 10-in. propeller, and the horizontal steam pipe disposed diagonally across the dye vat. Both machines were investigated.

COMMENTS ON MACHINES

The capacity of the cone dyeing machine is limited, the maximum load of the largest machine being 24 dozen hoods. Skilled labour is required for loading the hoods on the cones and fitting them into the machine. Penetration is rapidly achieved by the pumping of the dye liquor through the felt; hence the dyeing time is short and the consumption of steam and power is low.

The Cassé dyeing machine is much more economical with respect to labour costs, but does not permit such ready penetration as the cone dyeing machine. Machines capable of dealing with 6–30 dozen hoods are available. The Crescent machine is rather similar as regards operating costs; the advantageous feature is its size. Only one size, of capacity 340 gal., suitable for loads of 25–40 dozen hoods, is manufactured, but satisfactory arrangements have been made to couple two machines together, thus enabling up to 80 dozen hoods to be dyed simultaneously to one shade.

The Hudson rotary-drum machine is used mainly for dyeing wool-felt hoods, and is a highly satisfactory bulk-production unit for felt of low or medium density. The number of hoods that can be dyed is 30–100 dozen according to the size of machine and the weight of hoods. If material is dyed when barely felted, some felting action will occur during dyeing. Labour charges are moderate, except when tightly felted hoods are dyed and have to be turned inside out midway through the process to promote levelness.

The Obermaier is a small-capacity machine, the largest of which will dye 30 dozen 5-oz. hoods. Steam consumption is rather high, and a longer time is required to penetrate the felt than on the cone and Cassé machines.

Although a number of papers [2–6] relating to the dyeing of hats have been published in recent years, only Tucker [7] has reported detailed results comparing one machine with another with respect to felt quality. He used tensile strength and flexing value as the measures of felt degradation during dyeing. The machines investigated were a multiroller, a rotary cylinder (identical with the rotary-drum type employed in Great Britain), a cone, and a Mezzera (similar to the Cassé). The best results were obtained by dyeing on a multiroller machine whilst felting proceeded, and the worst by dyeing in a cone dyeing machine at the boil. The results were so much at variance with the experience of many British hat manufacturers, so far as the effect of dyeing in a cone machine is concerned, that an additional motive was provided for pursuing the objective of determining the effect of the dyeing machine on felt quality.

Three principal variables can be postulated as being the dominant factors influencing felt quality during dyeing—

(1) Time of dyeing

(2) Degree of agitation (the machine factor)

(3) Temperature of dyeing.

Within the limits of normal production, variations in colour, acid, and auxiliary additions are relatively minor factors, although they must be taken into account in making comparisons.

Experimental

The above three factors were therefore investigated. In the major experiment, in which different qualities of fur felt and wool felt were dyed in the various machines to light, medium, and heavy depths, time and temperature of dyeing were governed by the exigencies of factory productivity. The experimental work was carried out in factories, no effort being made to change the normal dyeing procedure. A number of standard hoods were dyed along with bulk lots, and the conditions of dyeing were noted. It was soon confirmed that time and temperature were of considerable importance; consequently, experiments were carried out to assess the influence of each on the change of felt quality during dyeing. The assessment of quality was based on a comparison of the strength and the density of the felt before and after dyeing. The influence of weight and volume changes in contributing to change in felt quality was analysed.

MATERIALS AND TESTING METHODS

Several qualities of fur-felt hoods were used in the experiments. The felt hat industry uses a wide variety of rabbit furs in the manufacture of its range of products. The best-quality hats are made from hare's fur or from selected fur from wild rabbits. BCBKS fur (Best Centre Backs) is recognised in the trade as being the best quality of fur. Of slightly lower quality is BCB Entire fur, and as it is widely used to make a good-quality fur-felt hat, it was used for the first series of trials. It is usual to include fur from the tame rabbit, such as Petit Bon fur, in blends for less expensive fur-felt hats. To ascertain the effect of dyeing such felt, a repeat experiment was carried out on selected machines.

A further variable is the type of carrotting preparation given, this being a chemical treatment to facilitate the subsequent felting of fur on acid milling. There are two varieties of carrotting preparations—mercuric, utilising mercury salts and nitric acid; and non-mercuric, employing hydrogen peroxide or other oxidising agent with acids and/or metal salts other than mercury. The use of non-mercuric carrotting treatments is becoming more popular in the United Kingdom, and in view of the need to process non-mercuric-carrotted fur felt under less acid conditions at lower temperatures than mercuric-carrotted fur felt, it was decided to compare the effect of the dyeing process (in selected machines) on each type of felt. During the course of the experiments, the opportunity was taken to observe the affect of dyeing wool-felt hoods in each machine.

Raw Materials

The relevant information concerning the standard hoods is as follows—

(i) GOOD-QUALITY FUR-FELT HOODS—Fully planked* 3½-oz. fur-felt hoods made from mercuric-carrotted BCB Entire fur.

(ii) POORER-QUALITY FUR-FELT HOODS—Fully planked 3½-oz. fur-felt hoods made from a mercuric-carrotted unspecified fur blend containing Petit Bon fur.

(iii) NON-MERCURIC-CARROTTED FUR-FELT HOODS—Fully planked 3½-oz. fur-felt hoods made from non-mercuric-carrotted BCB Entire fur. Hoods of comparable quality characteristics made from the same fur treated by a mercuric carrott were used in the same experiments for comparison. These hoods were also used in the temperature-range experiment.

(iv) WOOL-FELT HOODS—Fully planked 4¼-oz. wool-felt hoods made from a blend of 64/70s wool and noils in the proportion of 20% Cape wool and 80% Noble and Schlumberger combed Cape and Australian noils.

Where there was any departure from the use of such standard hoods, this is mentioned in the detailed account of the experiments below, together with a description of the hoods actually used.

Methods of Testing

The methods of obtaining test samples and the physical testing methods used were as devised by Baines and previously described by Barr and Haigh [10].

In all experiments acid levelling dyes were used.

EFFECT OF DYEING IN VARIOUS DYEING MACHINES ON THE QUALITY OF FELT

After careful conditioning and weighing, three standard good-quality fur-felt hoods were dyed to light, medium, and heavy depths, in each of the machines under test. In one factory, the cone dyeing machine was operated at the boil, but in another factory the highest temperature was controlled at 85°C. Each of the other machines was operated at the boil. After dyeing, the hoods were re-conditioned, the change in weight was calculated, and their physical properties were measured. The conditions and the times of dyeing are summarised in Table I together with the quality data.

The experiment was repeated on standard fur-felt hoods of a lower quality by carrying out similar dyeings in the cone, the F.T.M. Crescent, and the Cassé dyeing machines. Simultaneously three standard wool-felt hoods were dyed. In addition, similar dyeings were carried out on standard wool-felt hoods in a rotary-drum dyeing machine. The results of the quality assessment are given in Table II together with the dyeing data.

A further experiment was carried out in the cone and the Cassé machines by dyeing three mercuric-carrotted and three non-mercuric-carrotted fur-felt hoods within bulk lots to light and heavy depths in each machine. The results of the quality determinations are given in Table III together with the dyeing data.

* Reference is made to a "Short Glossary of Some Terms used in Wool Felt Hat Manufacture" [9] for an explanation of the technical terms peculiar to the industry.

TABLE I

Dyeing Data and Quality Factors for Hoods made from Good-quality Fur in Various Dyeing Machines

Dyeing Machine	Depth (%)	Dyeing Data: Final pH	Time of Dyeing: Total (min.)	Time of Dyeing: Boiling (min.)	Change in Wt. during Dyeing (%)	Quality Factors: Thickness (0·001 in.)	Quality Factors: Density (oz./cu.in.)	Quality Factors: Strength (lb./sq.in.)
Undyed	0	—	0	0	—	80·6	0·192	802
Cone	2·5	2·57	105	75	−1·7	84·0	0·188	722
	13·1	2·38	80	60	+3·2	80·7	0·206	801
	24·2	1·96	80	60	+7·4	83·4	0·212	810
Cone (at 85°C.) ...	2·4	2·15	90	80*	−1·9	78·8	0·191	831
	5·9	2·00	90	80*	−1·8	79·1	0·194	819
	36·7	1·90	95	80*	+5·7	79·6	0·203	853
Crescent	1·5	2·13	135	75	−1·3	87·6	0·183	728
	2·1	2·68	160	120	−1·3	88·6	0·182	715
	29·3	3·50	130	90	+0·5	85·0	0·186	745
Rotary-drum ...	4·3	3·25	135	85	−1·8	86·8	0·183	718
	5·2	2·98	180	120	−1·2	86·4	0·183	741
	26·3	3·34	185	115	+5·2	88·5	0·187	733
Obermaier	2·4	2·72	185	125	−2·3	86·7	0·184	698
	6·4	2·50	160	100	−1·0	87·9	0·184	728
	21·8	2·64	160	100	+5·3	91·5	0·190	703
Obermaier (modified)	1·9	2·56	105	30	−2·0	89·8	0·179	701
	11·7	2·70	155	80	−0·9	86·6	0·183	707
	20·7	2·70	105	30	+2·7	91·4	0·187	716
Cassé	1·5	4·24	90	75	−2·6	87·0	0·185	705
	4·8	4·24	100	85	−1·9	87·2	0·180	659
	21·2	2·48	120	105	+1·6	92·5	0·185	704

* Not at the boil

TABLE II

Dyeing Data and Quality Factors for Hoods made from Lower-quality Fur and for Wool Hoods in Various Dyeing Machines

Depth (%)	Dyeing Data: Final pH	Time of Dyeing: Total (min.)	Time of Dyeing: Boiling (min.)	Lower-quality Fur-felt Hoods: Change in Wt. during Dyeing (%)	Lower-quality Fur-felt Hoods: Quality Factors: Thickness (0·001 in.)	Lower-quality Fur-felt Hoods: Quality Factors: Density (oz./cu. in.)	Lower-quality Fur-felt Hoods: Quality Factors: Strength (lb./sq. in.)	Wool Hoods: Change in Wt. during Dyeing (%)	Wool Hoods: Quality Factors: Thickness (0·001 in.)	Wool Hoods: Quality Factors: Density (oz./cu. in.)	Wool Hoods: Quality Factors: Strength (lb./sq. in.)
UNDYED											
0	—	0	0	—	99·8	0·161	692	—	130·0	0·166	695
CONE MACHINE											
2·1	2·57	85	60	−1·7	99·4	0·158	651	+0·4	137·0	0·153	616
24·2	1·96	70	60	+7·8	100·7	0·171	684	+10·2	130·0	0·189	779
CONE MACHINE (at 85°C.)											
1·2	2·60	80	75*	+0·3	91·5	0·162	735	+0·5	122·0	0·162	691
26·4	1·88	100	90*	+8·7	91·6	0·175	731	+8·6	114·0	0·180	790
CRESCENT MACHINE											
2·0	3·06	210	165	−3·0	102·1	0·156	591	−1·7	144·0	0·155	530
23·4	2·75	160	120	+2·2	101·6	0·163	643	+4·1	133·0	0·166	568
CASSÉ MACHINE											
3·1	3·17	90	65	−2·3	108·0	0·149	601	+0·5	141·0	0·154	547
23·5	2·19	90	75	+1·9	108·6	0·157	612	+4·8	142·0	0·166	615
ROTARY-DRUM MACHINE											
2·0	—	135	90	—	—	—	—	−1·2	139·0	0·157	600
10·8	—	120	90	—	—	—	—	+1·7	127·0	0·199	730

* Not at the boil

TABLE III

Dyeing Data and Quality Factors for Hoods made from Mercuric- and Non-mercuric-carrotted Fur in Various Dyeing Machines

Dye (%)	Dyeing Data: Final pH	Time of Dyeing: Total (min	Time of Dyeing: Boiling (min.)	Hoods from Mercuric-carrotted Fur: Change in Wt. during Dyeing (%)	Quality Factors: Thickness (0·001 in.)	Quality Factors: Density (oz./cu. in.)	Quality Factors: Strength (lb./sq. in.)	Hoods from Non-mercuric-carrotted Fur: Change in Wt. during Dyeing (%)	Quality Factors: Thickness (0·001 in.)	Quality Factors: Density (oz./cu. in.)	Quality Factors: Strength (lb./sq. in.)
UNDYED											
0	—	0	0	—	78·2	0·198	932	—	81·8	0·193	900
CONE MACHINE											
4·1	2·35	95	70	−0·4	77·4	0·199	900	−0·8	79·8	0·204	857
18·3	2·23	75	50	+4·6	78·6	0·204	934	+3·0	81·1	0·211	848
CONE MACHINE (at 85°C.)											
0·9	2·10	80	70*	+0·3	77·2	0·194	882	+0·4	77·2	0·206	877
20·0	1·79	100	90*	+9·8	77·8	0·210	945	+8·2	79·6	0·218	867
CASSÉ MACHINE											
3·1	3·68	95	85	−1·8	83·4	0·185	751	−2·3	86·6	0·189	527
23·6	2·40	95	85	+2·3	84·9	0·191	820	+0·3	85·9	0·196	609

* Not at the boil

TABLE IV

Quality Factors of Fur-felt Hoods dyed for Different Times

	Quality Factors of Hoods: Thickness (0·001 in.)	Density (oz./cu.in.)	Strength (lb./sq.in.)
Undyed	63·2	0·148	683
At boil	72·8	0·159	664
Boiled for 30 min. ...	70·9	0·153	583
Boiled for 60 min. ...	71·6	0·151	596
Boiled for 90 min. ...	71·4	0·149	564
Boiled for 120 min. ...	75·1	0·147	539

A preliminary examination of the results was sufficient to indicate that the functions of time of dyeing and temperature of dyeing should be further investigated, whilst every other variable was maintained constant in each instance. Lightweight (2¾-oz.) hoods made from a lower-quality mercuric-carrotted fur blend including Petit Bon fur were dyed navy (6·5% Xylene Navy Blue HWD (S) + 1·25% Carmoisine conc. (S) (*C.I.* 179)) by normal factory dyeing methods in a Cassé dyeing machine. After boiling had commenced, and at half-hourly intervals, hoods were removed from the dyebath for test. A comparable undyed hood was also tested for quality (Table IV).

The temperature-range experiment was carried out in a single cone machine, at each of the following temperatures— (*a*) 100°C., (*b*) 90°C., and (*c*) 80°C. Each batch of hoods was made up of three standard hoods made from mercuric-carrotted fur and three from non-mercuric-carrotted fur, and given identical treatment except for the difference in dyeing temperature. A brown—

1·0% Kiton Fast Yellow 2G (CDC) (*C.I.* 639)
1·0% Kiton Fast Red R (CDC)
1·5% Alizarine Sapphire Blue 4G (CDC)

was dyed at 5 lb./sq.in. for 1 hr. The results are in Table V. To ascertain whether dyeing at temperatures lower than boiling resulted in any reduction in wet fastness, the Society's tests for fastness to water and perspiration[11] were carried out on patterns cut from the dyed hoods. It was evident that wet fastness was not impaired, but that there was a tendency for slightly improved results to be obtained by dyeing at the lower temperatures.

Discussion of Results

It was apparent from the first scrutiny of the results given in Tables I–III that felt hoods of better quality could be obtained by dyeing in the cone dyeing machine than in any of the circulatory

TABLE V

Dyeing Data and Quality Factors of Hoods made from Mercuric- and Non-mercuric-carrotted Fur dyed at Different Temperatures on a Cone Dyeing Machine

Type of Carrotting	Dyeing Data: Temp. (°C.)	Dyeing Data: Final pH	Time (min.)	Change in Wt. during Dyeing (%)	Quality Factors: Thickness (0·001 in.)	Quality Factors: Density (oz./cu.in.)	Quality Factors: Strength (lb./cu.in.)
Undyed ...	—	—	0	—	79·9	0·194	907
Mercuric ...	100	2·84	60	+1·1	81·0	0·192	819
	90	2·90	60	+1·6	78·0	0·198	854
	80	2·95	60	+1·9	77·9	0·195	885
Undyed ...	—	—	0	—	81·9	0·196	872
Non-mercuric	100	2·84	60	+0·4	77·5	0·206	721
	90	2·90	60	+1·6	77·0	0·205	884
	80	2·95	60	+2·1	77·3	0·204	878

machines, as in each instance tensile strength and density values were higher. The general trend was for hoods dyed in the cone machine to be as strong as, or slightly stronger than, and denser than comparable undyed hoods, whilst hoods dyed in any of the circulatory machines were weaker and less dense than undyed hoods. It was equally evident, when the results obtained on hoods dyed in a cone machine at 100°C. were compared with those dyed in a similar machine at 85°C., that better-quality felt could be obtained by dyeing at the lower temperature. Confirmation of this finding was obtained in the experiment carried out in a single cone machine under controlled conditions at different temperatures (Table V). The effect on hoods made from non-mercuric-carrotted fur was particularly marked, and emphasises the necessity for the most careful treatment possible of such hoods during dyeing as well as during processing. It was clearly shown (Table III) that such hoods are severely degraded when dyed in a Cassé machine at the boil, a reduction in strength during 90 min. dyeing time of approx. 40% being experienced.

The results obtained in the time-range experiment (Table IV) showed that degradation of felt during dyeing increased with time of dyeing. As there were considerable variations in dyeing time in different factories, and also for the different colours dyed within each factory, the influence of time of dyeing was examined in greater detail, together with an assessment of the influence of other variables such as pH of dyebath and dyeing recipe. It was considered necessary to examine the results given in Table I statistically to determine which of the factors involved predominated and influenced degradation significantly.

TENSILE STRENGTH

As indicated above, the obvious superiority of the cone dyeing machine with respect to effect on tensile strength could be due to the shorter dyeing time. The mean values for strength were, therefore, plotted against mean time of boiling during dyeing for each machine, and their relationship with the values obtained in the time-range experiment compared (Fig. 1). Assuming that a similar relationship exists for the heavier hoods as for the 2¾-oz. hoods dyed in the time-range experiment, it is seen that the cone machine enables stronger hoods to be obtained than does any other machine except the rotary-drum machine, even after taking into account the effect of boiling time.

The influence of depth of dyeing was next determined, but no definite relationships were evident when the individual results for strength were plotted against percentage depth. The results were therefore analysed by the method of variance analysis, the results for the cone machine being excluded because of their superiority. Indications that there were significant differences amongst the groups of circulatory machines were found, though a low result for the medium depth in the Cassé machine tended to emphasise the low values obtained on this machine and upset the variance

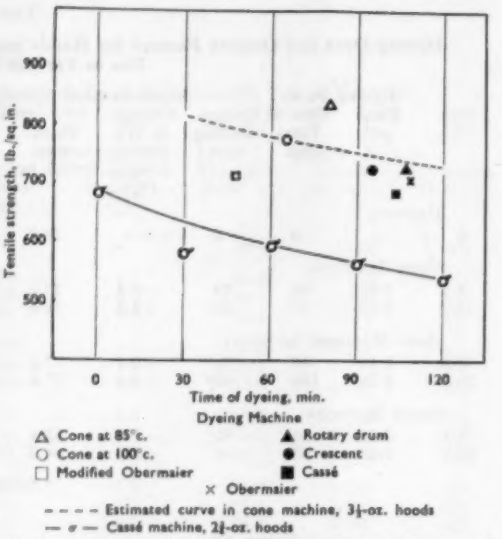


FIG. 1—Mean Values of Strength and Time of Dyeing for Hoods made from Good-quality Fur dyed in Different Machines

analysis. This result was excluded, and the analysis repeated. The results obtained showed that the values for tensile strength for felt dyed in the F.T.M. Crescent and the rotary-drum machines were significantly higher than those for felt dyed in the Obermaier and the Cassé machines. It was established, therefore, that the low result served only to emphasise trends which were already significant.

As there were no obvious reasons for this low result, the conditions were examined more critically, and were compared with those of the dyeing of the light shade in the same set, which was dyed in the identical machine. Apart from colour differences, the only other variable between the dyeings was that, to give comparable liquor ratios, different volumes of dye liquor were employed. As the agitation is caused by injection of dye liquor from a centrifugal pump, a much higher rate of flow would be obtained in the case of the deeper shade, where the vessel was half full, than with the light shade, where the vessel was two-thirds full. The dyeing conditions are summarised in Table VI. This result tends to show that the greater the degree of agitation of the dye liquor, the greater is felt degradation during dyeing.

Further evidence in support of this contention can be gleaned from a consideration of the strength values for hoods dyed in the Obermaier and modified Obermaier machines. In Fig. 1 it is evident that the mean values for strength are almost identical, despite a tremendous difference in time of boiling during dyeing. It would be expected from the estimated time-of-dyeing curve that the mean strength of hoods dyed in the modified Obermaier machine would be of the order of 780 lb./sq. in. It is likely that the increased agitation of the dye liquor caused by the larger propeller is responsible for the shorter dyeing time which is possible, but is also responsible for the low hood strength.

TABLE VI

Dyeing Conditions for Light and Medium Depths dyed in Cassé Dyeing Machine

Dyes	Light Depth	Medium Depth
Lissamine Fast Yellow 2G (ICI) (*C.I.* 639) ...	1·45%	4·81%
Lissamine Red 2G (ICI) ...		
Solway Blue PFN (ICI) ...		
Liquor ratio	40 : 1	40 : 1
Weight dyed	13·5 lb.	9·25 lb.
Volume of dye liquor	54 gal.	37 gal.
Capacity of vessel when full...	75 gal.	75 gal.
pH of exhausted dye liquor	4·24	4·42
Time of dyeing (boiling time)	75 min.	85 min.
Tensile strength	705 lb./sq.in.	659 lb./sq.in.

DENSITY

The graph of density and depth of dyeing indicates that the dyeing machines fall into two distinct groups, viz. package-dyeing machines and circulatory machines (Fig. 2). The density of felt dyed in the cone machine was higher at corresponding depths than that of felt dyed in any of the circulatory-type machines. It was possible to carry out a regression analysis of the results obtained from felt dyed in circulatory machinery, and a relationship between density and depth of dyeing was derived in which density increases with depth according to the following equation—

$$D = 0{\cdot}182 + 0{\cdot}00019S \qquad \text{(i)}$$

where D = density in oz./cu. in. and S = percentage depth, calculated on the basis of 100% commercial dyes.

No significant relationship was found between density and pH of dyebath or time of boiling. The residual variations after eliminating the effect of depth were not correlated with dyeing machine.

Using the value for initial felt density quoted in Table I (0·192 oz./cu. in.), equation (i) can be transposed into the form—

$$d = 0{\cdot}090S - 5{\cdot}2 \qquad \text{(ii)}$$

where d = percentage change in density.

In each instance in the series of experiments, there was a reduction in density during dyeing in circulatory machines. There were insufficient results for the density of cone-dyed felt to derive a satisfactory equation, but the positions of the points on the graph made it quite clear that the increase in density with increasing depth was greater than that expected from the weight changes. Consolidation of the felt, believed to be due to felt compression, occurs during dyeing in the cone machine.

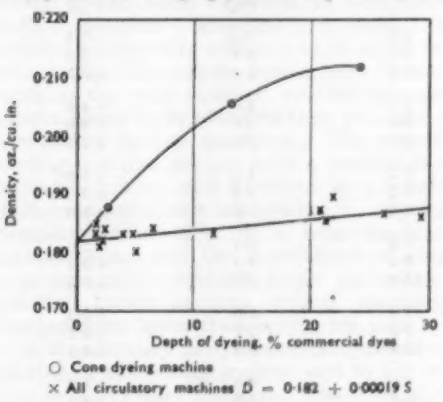


FIG. 2—Effect of Depth of Dyeing on Density

WEIGHT CHANGES

The recorded weight changes were plotted against the corresponding depth of dyeing (Fig. 3), and two separate linear relationships starting from the same origin were obtained. The one of greater slope was for the weight change–depth relationship for dyeings in the cone machine. The other line fitted the results obtained from dyeings in all the other dyeing machines. This provided further confirmation that, among the dyeing machines investigated, there are essentially only two types.

Regression analyses were carried out, and the following equations were derived—

$$W = 0{\cdot}41\ S - 2{\cdot}24 \text{ for the cone machine} \qquad \text{(iii)}$$

$$W = 0{\cdot}216\ S - 2{\cdot}24 \text{ for all other machines} \qquad \text{(iv)}$$

where W = percentage change in weight.

Each line cuts the axis at 2·24% weight loss, which can be regarded as representing the weight loss due to dissolution of protein and change in acid content of felt which would result by treatment in a "dyebath" with no dye present. In equation (iii) the constant 0·41 indicates that 41% of the dye added has been accounted for by increase in weight of felt, after taking into account the loss by protein solution, etc. Considering the uncertainty

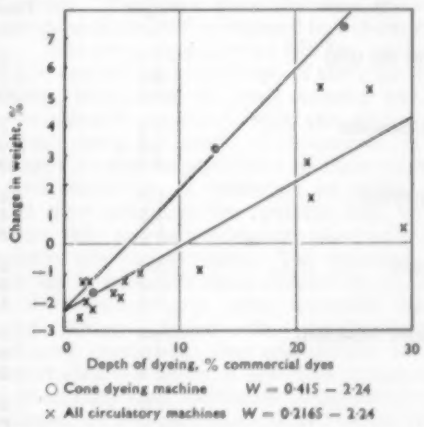


FIG. 3—Effect of Depth of Dyeing on Change in Weight

of the strength of the commercial dyes used, and the degree of exhaustion obtained, the weight changes obtained agree reasonably with those expected. In the case of all the circulatory machines, however, a low rate of weight increase in relation to the amount of dye added is obtained. Equation (iv) indicates that the weight increase of the felt is only 21·6% of the weight of commercial dye added. This is to be examined in greater detail. After the effect of depth of dyeing had been eliminated, there was no correlation between variation of weight and dyeing machine.

Comparing equations (ii) and (iv), it is noted that the constant term 5·2 in the density equation is greater by approx. 3·0 than the constant term in the weight change equation for circulatory machines. This means that there is a reduction in density of 3% during dyeing in circulatory machines, not attributable to protein solution or loss of acid, and although dye uptake partly compensates for this, a 30% depth would need to be dyed to restore the density to that of similar undyed felt. This density reduction during dyeing is generally known as felt "opening-out". The increase in density with increasing depth is less than half that expected from the weight changes, and suggests further opening-out proportional to depth of dyeing. The precise mechanism of felt opening-out on dyeing is still unknown.

It seemed likely that either opening-out or compression of felt would be more clearly shown by computation of the volume changes of the felt which occur during dyeing. In Table VII the changes in weight, density, and thickness of the hoods during dyeing have been worked out from the data of Table I. From these results the changes in volume and in area were calculated. The volume changes confirmed the differences between the two types of machine. The package-dyeing type of machine (the cone) caused compression of felt, resulting in a reduction in volume during dyeing. All the circulatory machines caused increase in volume, associated with felt opening-out. The greater the depth of dyeing, the greater was the volume of dyed felt. No single equation satisfying this relationship for all the circulatory machines could be found, however, owing to the scatter of the results. The relationship seems different for each machine, but time of boiling during dyeing does not account for these differences.

The results shown in Tables II and III were not subjected to statistical analysis, as they were seen to substantiate the findings already indicated. The dyeings in the F.T.M. Crescent machine (Table II) were unfortunately of long duration, owing to matching difficulties; consequently, rather poor results were obtained on the hoods made from the lower-quality fur and the wool hoods in this machine.

Summary and Conclusions

Three major factors are shown to influence the degradation (or loss of quality) of felt hoods on being dyed under practical conditions. These are—

(1) Machine in which dyed
(2) Length of time of dyeing
(3) Temperature of dyeing.

Degradation is measured by a reduction in tensile strength or density and strength during dyeing. Factors contributing towards this degradation include increase of volume of felt ("opening-out"), loss of dissolved protein, modification of the remaining fibres, and dye uptake. It is feasible that any reduction in density by "opening-out", by fibre solution, or by both will give a proportional reduction in strength. Modification of the remaining fibres probably reduces strength to a greater extent than it reduces density. The

TABLE VII

Changes in Dimensions of Hoods during Dyeing in Various Machines

(Compiled from data in Table I)

Dyeing Machine	Change in Weight (%)	Change in Density (%)	Increase in Thickness (%)	Reduction in in Area (%)	Change in Volume (%)
Cone (at the boil) ...	−1·7	−2·1	4·2	3·5	+0·4
	+3·2	+7·3	0·1	3·9	−3·8
	+7·4	+10·4	3·5	5·8	−2·6
F.T.M. Crescent ...	−1·3	−5·2	8·7	4·0	+4·3
	−1·3	−4·7	9·9	5·6	+3·6
	+0·5	−3·1	5·5	3·6	+3·7
Rotary-drum ...	−1·8	−4·7	7·7	4·2	+3·0
	−1·2	−4·7	7·2	3·2	+3·7
	+5·2	−2·6	9·8	1·6	+8·0
Obermaier	−2·3	−4·2	7·6	5·1	+2·0
	−1·0	−4·2	9·1	5·1	+3·4
	+5·3	−1·0	13·6	6·0	+6·5
Obermaier (modified)...	−2·0	−6·8	11·4	5·5	+5·2
	−0·9	−4·7	7·5	3·1	+4·1
	+2·7	−2·6	13·4	6·9	+5·5
Casaé	−2·6	−3·7	8·0	6·3	+1·2
	−1·9	−6·3	8·2	3·3	+4·7
	+1·6	−3·7	14·8	8·0	+5·6

influence of dyes is complex, and is to be the subject of further study.

The circulatory type of dyeing machine has been shown to have a worse effect on felt quality than the package-dyeing type. The detailed analysis of the results given in Table I indicates some of the reasons for the difference in performance. In the cone dyeing machine, felt compression contributes towards preservation of quality by increasing density. Strength is consequently maintained at a relatively high value. The weight changes of the felt during dyeing, which are proportional to the amount of dye added, are also in agreement with those expected after taking into account the actual strength of the commercial dyes, the degree of exhaustion of dyes, and dissolution of protein. In each of the circulatory machines, considerable protein solution, fibre modification, and felt volume increase occur during dyeing, resulting in reduction in quality. The extent of this depends on the agitation of liquor and hoods in the machine. The calculated volume changes indicate that "opening-out" also tends to increase with increasing depth of dyeing. The weight changes of the felt during dyeing, though proportional to depth, are much smaller than in the cone machine, and cannot be explained in terms of dye strength or degree of exhaustion of dyebath.

The influence of time of dyeing is simple: the longer the duration of dyeing, the greater is felt degradation. Strength and density both decrease with increasing time, but strength is reduced to a greater extent than density, suggesting that fibre modification, as by acid hydrolysis, etc., accompanies opening-out of felt and solution of protein.

In cone dyeing machines the influence of dyeing at temperatures lower than boiling was beneficial with respect to quality without impairing fastness. Adequate penetration is quickly achieved in this type of machine, as the dye liquor is forced, under pressure, through the felt. Thus there are no difficulties in ensuring penetration when dyeing at temperatures of 80°C. or 90°C. The possibilities of reducing dyeing temperature in the circulatory machines are to be investigated, though it is anticipated that levelness and penetration will not be so readily achieved at 80°C. or 90°C. as at the boil.

The investigation has clearly shown the danger of dyeing felt made from non-mercuric-carrotted fur at the boil in circulatory machinery, where considerable hood movement is possible during dyeing. A reduction in strength of approx. 40% during 90 min. dyeing time is far in excess of what can be tolerated.

The following conclusions can be drawn from the results obtained—

(1) With increasing dyeing time, there is increasing felt degradation.

(2) Only dyeing machinery which enables penetration to be obtained quickly without opening-out the felt is suitable for preserving the quality of all types of felt hoods during the dyeing process. The cone dyeing machine fulfills these requirements. Of the circulatory machines, the best results are given by those in which there is the least movement of hoods relative to each other.

(3) It is advantageous to dye at temperatures lower than 100°C., especially when dyeing hoods made from non-mercuric-carrotted fur. This is possible in cone dyeing machinery, as penetration and levelling problems are not difficult. To obtain similar advantages on other machinery, methods should be sought enabling well penetrated, level uptake of dye to take place from the start of dyeing.

(4) It is inadvisable to dye hoods made from non-mercuric-carrotted fur in circulatory machinery at the boil, because of the high degradation obtained.

II—An Investigation into Wool-felt Dyeing

Introduction

The opportunity has been taken to extend the work described in Part I by determining the effect of the same variables on the quality of fully planked standard wool-felt hoods. Similar results were obtained to those on fur felt: the use of the package-dyeing type of machine, such as the cone machine, enabled stronger and denser hoods to be obtained than with any of the circulatory dyeing machines. The rotary-drum dyeing machine did not have a marked effect on wool-felt quality, and its choice as a satisfactory bulk-production unit was confirmed. Dyeing at a temperature of 85°C. in a cone machine was advantageous, and the possibilities of obtaining superior-quality wool-felt hoods by dyeing fully planked hoods in cone dyeing machinery at temperatures lower than boiling are good.

It is customary to dye wool felt before the completion of the felting process, and to felt to final size in heavy-duty bumpers. The work reviewed above indicated one variation from this procedure likely to lead to an improvement in felt quality, viz. by dyeing fully felted hoods in package-dyeing machinery. The shape is not distorted, and ready penetration of the felt is obtained in a short dyeing time. The economics of wool-felt hat production militate against the regular use of the cone dyeing machine, because of its small capacity and high labour charges compared with the rotary-drum machines normally used. Consequently, it was necessary to seek improvement in other ways. It seemed likely that a reduction in dyeing time would give enhanced felt quality, but how to achieve this and get adequate penetration and levelness was the problem. The penetration of dense felt is very difficult in circulatory machines, and is achieved only after relatively lengthy dyeing times. Before the development of machinery permitting the penetration of half-planked wool-felt hoods, it had been customary to dye at an early stage during the sequence of felting processes. It was therefore decided to investigate the effect on felt quality of dyeing at different

stages of felting, it being recognised at the outset that the earlier that dyeing could take place, the more easily would felt penetration be attained and the shorter the dyeing time. It is, of course, necessary to apply dyes which will not be affected by the acid conditions of subsequent felting operations if dyeing at an early stage of processing is to be feasible. The most suitable dyes are the acid milling or chrome types, and the effect on felt quality of dyeing wool felt with such types of dye was therefore determined. An experiment was conducted to demonstrate whether or not increasing dyeing time is detrimental to wool felt quality.

All these laboratory experiments were carried out on wool-felt patterns produced in the Furness experimental milling stocks[12], which is highly suitable for such work. This machine has been examined by Davidson[13] with a view to its use in drawing up a standard for the estimation of milling shrinkage. Under certain operating conditions he found that reproducible results "between runs" were obtainable. These conditions were fulfilled in each of the experiments reported.

The results of two factory trials based on the findings of the laboratory experiments are reported. Further work is proceeding to determine the optimum conditions of dyeing and the best stage of processing at which to dye.

Experimental

RAW MATERIALS AND TEST METHODS

Materials

In each instance in the laboratory experiments, standard wool-felt patterns made from a blend of 64/70s wool and noils were used. The blend contained 20% Cape wool and 80% Noble and Schlumberger-combed Cape and Australian noils. Hardened flats were prepared from this material by carding the wool and noils on a factory opener carding machine and then passing through a hatter's card, whence the issuing web was wound on to a revolving drum until 4 oz. of web was on the drum. The cylindrical form was cut to yield a flat 24 in. square, which was then hardened on a Garside flat-hardening machine.

Felting

Squares, of side 6 in., were cut from each hardened flat, and these were felted or dyed as required. In each experiment the number of hammer blows given in the Furness milling stocks was identical for each set of patterns, whether undyed or dyed. The patterns were soaked for 48 hr. in acid of the appropriate pH before felting. The requisite number of patterns to make up a weight of 5¼–6 oz. were used in each lot, and were introduced into the stocks, which operated at 60 hammer blows per minute. The machine was fitted with a positive release mechanism and stainless-steel lining described by Davidson[13] as being desirable. After every 600 hammer blows, the patterns were removed, straightened, and turned horizontally through an angle of 90°, redipped in the equilibrium acid liquor, and then returned to the machine. This treatment reduced the incidence of directional effects from mechanical influences.

Physical Measurements on Felt

Only one test sample could be obtained from each pattern. To avoid any influence by directional effects[14], each sample was cut diagonally from the pattern. The physical testing methods used were as devised by Baines and described by Barr and Haigh[10]. Where an estimate of the shrinkage of test patterns was required, it was calculated from planimeter measurement of the area of test patterns at various stages of felting. Patterns were carefully straightened out, without stretching the felt, and interposed between two glass plates for measurement.

EFFECT ON QUALITY OF DYEING WOOL FELT AT VARIOUS STAGES OF FELTING

An experiment was devised which sought to establish the effect on wool-felt quality by dyeing at various stages of felting in the Furness experimental milling stocks. Comparison with a similar set of undyed patterns was made.

For this purpose, five sets of hardened flat-felt wool patterns, made from a standard blend, were each soaked in sulphuric acid solution of initial pH 2·0 before each period of felting (by a total of 21,000 hammer blows in the Furness stocks) as follows—

Set A— Undyed
Set B— Dyed with acid milling dyes and then felted
Set C— Dyed after 7,000 blows, and felting completed by a further 14,000 blows
Set D— Dyed after 14,000 blows, and felting completed by a further 7,000 blows
Set E— Felted and dyed.

Dyeing was carried out for 60 min. at the boil with 0·8% Cloth Fast Brown RN (CDC) + 0·15% Cloth Fast Green B (CDC), with 10% anhydrous sodium sulphate and 3% acetic acid. Where dyeing followed felting, the patterns were thoroughly washed in water prior to dyeing. No further efforts were made to promote levelness, as this was not a requisite of the experiment.

The above experiment was duplicated on patterns made from hardened wool-felt flats of unknown composition (Felt II). Quality determinations were carried out on patterns from each type of felt, with the results given in Table VIII. The area shrinkage determinations were of little significance when considered in relation to the quality factors, but are of interest in showing the shrinkage after each stage in the experiment. For example, the undyed patterns made from the standard wool blend had shrunk 37·4% of their original area after 7,000 blows, 46·7% after 14,000 blows, and 53·3% after 21,000 blows. It is recognised that this is less than is achieved in the bulk processing of wool-felt hoods, but further felting in the experimental stocks could not be carried out or the patterns would have been too small to permit a standard test sample to be cut. Larger unfelted patterns cannot be used, because the bowl of the machine will not accommodate them satisfactorily.

TABLE VIII

Quality Factors of Wool Felt Patterns dyed at Various Stages of Felting

	Felt I (Standard)			Felt II		
	Thickness (0·001 in.)	Density (oz./cu.in.)	Strength (lb./sq.in.)	Thickness (0·001 in.)	Density (oz./cu.in.)	Strength (lb./sq.in.)
Undyed	125·2	0·136	591	96·7	0·135	580
Dyed before felting	116·7	0·142	659	97·8	0·142	590
Dyed after 7,000 blows ...	117·9	0·141	619	99·4	0·141	582
Dyed after 14,000 blows ...	108·9	0·136	567	96·2	0·134	558
Dyed after 21,000 blows ...	126·8	0·135	550	107·1	0·130	503

This limitation detracts little from the value of the results, which clearly indicate that the best quality of wool felt is obtained by dyeing at as early a stage as possible, i.e. as hardened felt. The tensile strength and the density of the fully felted material dyed at this stage were equal to, if not better than, those of undyed felt.

INFLUENCE ON SHRINKAGE RATES AND QUALITY OF WOOL FELT OF DYEING WITH VARIOUS TYPES OF DYES BEFORE FELTING

Having established that improvement in quality is possible by dyeing at an early stage of felting, it was desirable that the influence, on felt shrinkage and quality, of the possible types of dye capable of giving adequate fastness to acid milling should be assessed. Although Neolan (premetallised) dyes are no better than levelling acid dyes with respect to acid milling fastness, they do possess better light and water fastness properties, and were included in the experiment for this reason.

Patterns cut from six hardened flats were equally apportioned amongst six experiments, after being soaked to equilibrium pH value in successive lots of tap water, followed by distilled water. Six sets, each containing sixteen patterns, were then respectively treated as follows—

1. Undyed

2. Dyed for 1 hr. at the boil with acid dyes—
   0·8% Xylene Light Yellow 2G (S) (*C.I.* 639)
   1·0% Kiton Red G (CDC) (*C.I.* 31)
   0·5% Solway Blue BNS (ICI) (*C.I.* 1054)
   with 10% Anhydrous sodium sulphate + 3% sulphuric acid
   Final pH of dye liquor 2·66

3. Dyed for 1 hr. at the boil with acid milling dyes—
   0·8% Cloth Fast Brown RN (CDC)
   0·15% Cloth Fast Green B (CDC)
   with 10% Anhydrous sodium sulphate + 3% acetic acid
   Final pH of dye liquor 4·34

4. Dyed for 1 hr. at the boil with premetallised dyes—
   1·0% Neolan Yellow BE (Ciba and CDC)
   0·9% Neolan Red BRE (Ciba and CDC)
   0·5% Neolan Blue GG (Ciba and CDC)
   with 8% sulphuric acid
   Final pH of dye liquor 1·78

5. Dyed with afterchrome dyes—
   0·9% Solochrome Brown EBS (ICI) dyed with 10% anhydrous sodium sulphate and 3% acetic acid for 30 min., followed by an addition of 0·5% formic acid for 15 min., and then afterchromed with potassium dichromate for a final 30 min. at the boil.
   Final pH of dye liquor 4·34

6. Boiled for 1 hr. in water.
   Final pH 4·97

After dyeing, the patterns were soaked to equilibrium in sulphuric acid solutions so that the final pH was approx. 2·35 in each instance. The sets were then felted separately in the Furness milling stocks for 10,800 hammer blows, the areas of six randomly chosen patterns from each being measured at intervals of 3,600 blows. The final area of each pattern was measured by planimeter, and the quality factors were determined by the standard procedure. The results are given in Table IX.

The quality of felt dyed with acid or acid milling dyes before felting was better than that dyed with Neolan (premetallised) or afterchrome dyes. The strongly acid conditions required for Neolan dyes

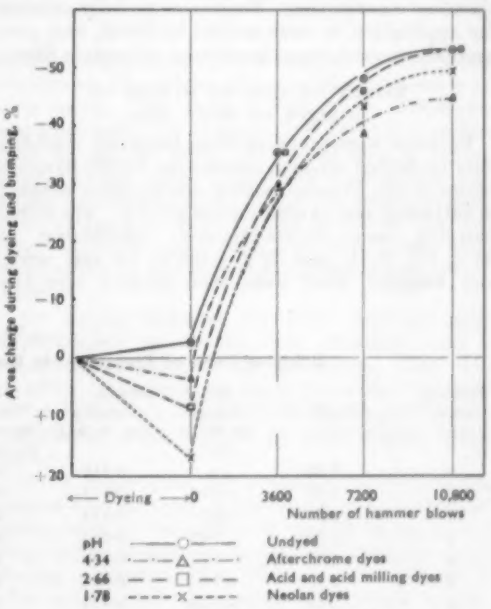


FIG. 4—Area Shrinkage of Dyed Patterns

TABLE IX

Effect of Dyeing by Various Methods before Felting on the Shrinkage and Quality of Wool Felt

Treatment	Shrinkage after 10,800 Hammer Blows		Quality Factors			Cr in Felt (% $K_2Cr_2O_7$)	Acid in Felt (% H_2SO_4)
	Calc. on Original Area (%)	Calc. on Area before Felting (%)	Thickness (0·001 in.)	Density (oz./cu.in.)	Strength (lb./sq.in.)		
Undyed	52·8	51·5	111·6	0·137	576	—	2·26
Boiled in water ...	52·5	52·2	107·3	0·146	522	—	2·22
Dyed with acid dyes	52·4	56·0	109·4	0·146	539	—	2·18
Dyed with acid milling dyes ...	53·5	54·7	118·7	0·141	542	—	2·28
Dyed with Neolan (premetallised) dyes	49·1	57·0	100·1	0·142	517	0·16	2·22
Dyed with afterchrome dyes ...	44·7	46·4	110·9	0·133	509	0·45	2·30

caused a considerable area increase in the patterns. The final area after felting was therefore greater than that of patterns dyed with acid or acid milling dyes, though the rate of shrinkage was comparable. Dyeing with afterchrome dyes caused some reduction in shrinkage rate, density, and strength of the patterns because of the effect of chromium ions on the elastic properties of the fibres[15]. In Fig. 4 the area-shrinkage curves are illustrated, and it is notable that the stronger the acid conditions of dyeing, the greater the area expansion during dyeing. The most promising type of dye examined was the acid milling type. A preliminary experiment, not reported in detail, in which Irgalan (Gy) (neutral-dyeing premetallised) dyes and Carbolan (ICI) dyes were also examined, indicated that the behaviour of each was like that of acid milling dyes, and they were subsequently regarded as being of that type though of different chemical constitution. They are especially suitable for application to near-neutral material, and give good all-round fastness properties on protein fibres.

EFFECT OF TIME OF DYEING ON QUALITY OF WOOL FELT

Patterns were prepared from hardened wool-felt flats by felting six-inch squares for 12,000 hammer blows in the Furness milling stocks, after soaking in sulphuric acid of equilibrium pH 2·2. The felted patterns were hydroextracted, conditioned at 65 ± 1% R.H. and 22·2 ± 0·5°c. for one week, and weighed. They were then divided into two lots of sixteen and treated for various times in—(*a*) a boiling "blank" dyebath containing 10% anhydrous sodium sulphate and 2·5% sulphuric acid, calculated on the weight of material; and (*b*) a boiling dyebath containing similar quantities of salt and acid, and—

1·25% Xylene Light Yellow 2G (S) (*C.I.* 639)
1·25% Kiton Red G (CDC) (*C.I.* 31)
2·5% Solway Blue BNS (ICI) (*C.I.* 1054)

After treatment, the patterns were hydroextracted, reconditioned for one week at standard humidity and temperature, reweighed, and tested for felt quality. The boiling treatments, with and without dye, were carried out under reflux at a 50 : 1 liquor : goods ratio. The initial and final pH values of the bath were determined by means of a glass electrode. The results are given in Table X.

As dyeing or boiling time increased, there was progressive loss in weight and strength. The patterns showed little change in density beyond an initial reduction. There was no significant difference between a normal dyebath and a blank dyebath with respect to reduction in felt strength. The only difference with respect to weight was that the uptake of dye partly compensated for protein loss.

DISCUSSION OF LABORATORY EXPERIMENTS

The laboratory experimental work has shown that, by dyeing at as early a stage as possible during the felting operation, the quality of wool felt can

TABLE X

Effect of Time of Treatment in Boiling Dyebath on Quality of Wool Felt

Boiling Time (hr.)	Blank Dyebath				Dyebath			
	pH	Change in Wt. (%)	Density (oz./cu.in.)	Tensile Strength (lb./sq.in.)	pH	Change in Wt. (%)	Density (oz./cu.in.)	Tensile Strength (lb./sq.in.)
0	2·20	—	0·118	555	2·25	—	0·120	530
½	2·22	+0·02	0·114	510	2·31	+1·00	0·114	526
1	2·23	−0·11	0·114	483	2·31	+0·92	0·115	485
2	2·25	−0·43	0·114	463	2·34	+0·49	0·117	450
3	2·27	−0·87	0·115	422	2·36	+0·21	0·116	447
4	2·28	−1·18	0·114	408	2·38	−0·24	0·116	410
5	2·30	−1·79	0·114	364	2·39	−0·39	0·118	393
6	2·32	−2·38	0·116	356	2·40	−1·23	0·117	352

be improved. The best type of dye examined from the point of view of effect on felt quality and fastness requirements was the acid milling type (including Carbolan, Irgalan, etc.). The influence of time of dyeing on felt quality is that the shorter the time of dyeing, the better is quality. By combining these three findings, so that wool felt is dyed for a short time with acid milling dyes after settling, the optimum quality should be obtained.

Wool-felt hoods are produced from hardened forms by the application of compression and frictional forces under conditions of weak acidity. The felting processes given gradually increase in severity. Settling is the first planking process, normally carried out in four-roller settling machines or in multiroller sets. The settled hoods are then bumped in light-duty stocks until they have shrunk to a given size, often 1–1½ in. higher and wider than the fully planked hood. It is customary to dye at this stage, and then to shrink the hoods to their final size in heavy-duty stocks. Considerable variation between different factories has been noted, but a typical reduction of hood area during processing is given in Table XI.

TABLE XI

Change in Area of a 3½-oz. Wool-felt Hood during Processing

Stage	Area (sq. in.)	Total Shrinkage (%)
Before hardening ...	353	—
After hardening ...	337	4·7
After settling ...	278	21·3
After "white" bumping	155	56·1
After dyeing ...	156	55·8
After "colour" bumping	133	62·3

In the first experiment described, the standard wool blend shrunk 37·4% of its original area during 7,000 blows in the stocks. This is appreciably greater than the shrinkage which a wool form undergoes on settling (21·3%) as shown in Table XI. The best results were obtained by dyeing hardened felt, but in bulk production it is not advantageous to dye hardened material in rotary-drum dyeing machines owing to the felting action which takes place.

It is possible to settle the material, however, or even bump the felt slightly and still obtain most of the advantages of dyeing at an early stage of felting. Such treatment is sufficient to avoid the felting action in the dyeing machine. The settling process is normally carried out in warm water (50°C.) in settling machines or multirollers, but the hardened forms are soaked previously in acid to near equilibrium.

If felt were dyed with the acid milling type of dye in this state, too rapid exhaustion of the dye, with attendant unevelness, would occur. Possible methods of avoiding these difficulties would be to settle the felt in warm water only and soak to equilibrium in acid of the appropriate strength after dyeing, or preferably to add the requisite amount of acid to the completed dyeing to give the desired acidity of felt.

In the experiment reported above (Table VIII) the dyeing time was the same at whatever stage of felting the patterns were dyed. The penetration of hardened or settled felt is much more quickly achieved than that of fully or half planked material. It should be possible, therefore, to effect a reduction in dyeing time which should contribute towards a further improvement in felt quality.

FACTORY TRIALS

Some preliminary trials have been carried out in factories, and the results indicate that the experimental work is being confirmed under practical conditions.

The first trial reported had the objective of comparing the effects of dyeing at an early stage of felting with normal procedure. It is sufficient for this purpose to compare hoods after bumping. The normal sequence of processes used by this factory in the manufacture of wool-felt hoods is—

1. Forming
2. Hardening
3. Acid soaking
4. Four-roller settling
5. Multiroller settling
6. Bumping

The bumping process is carried out in three stages, and dyeing is usually done on completion of the second stage.

Three nominally similar batches of 45 dozen hardened forms (3¾ oz. form weight) were separately processed as follows to stage 6—

Batch 1. Dyed after seven passes through a four-roller settling machine, then given a further five passes to provide sufficient strength for bumping

Batch 2. Dyed after multiroller settling

Batch 3. Dyed at the normal stage, between bumping sequences.

Quality determinations were carried out on hoods withdrawn at various stages of the processing of each batch. The area of each hood withdrawn was measured, and is given in Table XII together with the quality data. The total time of felting given to each batch to the end of bumping was approximately the same. Since the area shrinkage after bumping was also similar, it follows that the stage at which the hoods were dyed had little or no effect on the shrinkage characteristics of the material.

By dyeing between or after settling runs, improvement in quality was obtained, and a reduction of 30 min. in the dyeing time was possible. No effort was made to change the type of dye in this experiment, level-dyeing acid dyes of moderately good fastness to acid milling being used.

Much fewer data are available concerning the second factory trial, which was a straightforward comparison of the effect of dyeing at an earlier stage in the bumping process. The stage at which dyeing normally takes place in this factory is after approx. 150 min. bumping (for 4½-oz. hoods). The minimum period of boiling during dyeing is

TABLE XII

Quality Factors and Processing Data of 3½-oz. Wool-felt Hoods dyed at Different Stages of Felting

	Batch 1				Batch 2				Batch 3			
	No. of Passes or Time in Machine	Area (sq.in.)	Density (oz./cu. in.)	Strength (lb./sq. in.)	No. of Passes or Time in Machine	Area (sq.in.)	Density (oz./cu. in.)	Strength (lb./sq. in.)	No. of Passes or Time in Machine	Area (sq.in.)	Density (oz./cu. in.)	Strength (lb./sq. in.)
Hardened and soaked...	—	397	0·096	293	—	406	0·089	255	—	412	0·093	304
Settling—												
Four-roller ...	7 passes	396	0·107	409	2 passes	463	0·099	321	2 passes	376	0·109	337
Multiroller ...	—	—	—	—	20 passes	381	0·112	538	20 passes	337	0·114	584
Dyed	105 min.	390	0·090	294	110 min.	368	0·109	376	—	—	—	—
Settled after dyeing	asses	349	0·118	457	—	—	—	—	—	—	—	—
Bumping—												
1st stage ...	40 min.	262	0·136	543	35 min.	248	0·139	514	45 min.	232	0·140	623
2nd stage ...	30 min.	216	0·148	562	35 min.	221	0·152	565	30 min.	202	0·145	665
3rd stage ...	35 min.	186	0·161	623	30 min.	192	0·163	616	—	—	—	—
Dyed	—	—	—	—	—	—	—	—	135 min.	201	0·148	546
Bumped after dyeing	—	—	—	—	—	—	—	—	30 min.	186	0·162	571

TABLE XIII

Quality Factors of 4½-oz. Wool-felt Hoods dyed at Different Stages of Felting

Time of Bumping before Dyeing (min.)	Boiling during Dyeing (min.)	Final Area (sq.in.)	Wt. (oz.)	Thickness (0·001 in.)	Quality Factors Density (oz./cu.in.)	Strength (lb./sq.in.)
			NORMAL PRODUCTION			
150	100	176	4·19	123·0	0·193	625
			SPECIAL BATCH			
60	55	183	4·26	125·1	0·187	700

100 min. when dyed at this stage. In the trial, one batch of hoods of form weight 4½ oz. made from a blend of wool and noils, such as were used in the laboratory experiments, was processed in the normal manner. A second batch was dyed after 60 min. bumping, and then colour-bumped to a similar size to the first batch; dyeing was completed after 55 min. boiling time in this instance. Hoods were submitted from each completed batch and were tested for quality by the standard procedure. The results are given in Table XIII and show that considerably stronger felt is obtained by dyeing earlier during processing.

Summary and Conclusions

The earlier in the felting sequence that wool felt can be dyed, the better is the quality of the resultant material. The performance of the dyeing machine dictates how soon dyeing can be carried out in practice. Acid milling dyes have less effect on feltability and felt quality than have Neolan (premetallised) or chrome dyes when applied at an early stage of felting. They compare favourably in this respect with levelling acid dyes, and have better fastness properties. As they are usually acid- or salt-sensitive, the felt must be near-neutral if level and well penetrated dyeings are to be obtained. This is much more readily achieved on lightly felted than on tightly felted material. The results indicate that the use of dyes of the acid milling type warrants further investigation. Wool felt loses weight and strength progressively with increase in time of dyeing, or boiling in a blank dyebath. It is advantageous to limit dyeing time as far as possible.

The results of the laboratory experiments indicate that the application of acid milling dyes at an early stage of felting, on almost neutral material for short dyeing times (less than an hour) should give optimum felt quality coupled with good fastness properties. The factory trials confirm that better felt quality is obtained by dyeing earlier than normal during the sequence of felting processes, and that considerable reduction in dyeing time can be effected. There are no results available yet on the effect of dyeing lightly felted material with acid milling dyes under bulk conditions.

* * *

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The Use of Fading Lamps for Determining Light Fastness

K. McLAREN

There are three possible causes of the significant differences sometimes experienced between fading-lamp and daylight fastness figures— spectral composition, temperature, and moisture content. Although there are marked differences between the spectral composition of fading lamps and sunlight, on theoretical grounds these would not appear to be the main cause of large discrepancies. The most likely cause is surface moisture content during exposure, and this depends on surface temperature and on the relative humidity of the surrounding air. It will be necessary to investigate these factors in detail before a specification for fading-lamp operation can be issued.

INTRODUCTION

The use of an artificial light source for light fastness determinations will always be necessary in cases where results have to be obtained much sooner than would be possible if daylight exposures were made.

The official method of determining light fastness, *B.S.*1006 : 1953, is, however, confined to daylight exposures, and, apart from a warning that fading lamps do give erroneous results in many cases, the only reference to their use is the recommendation that the degrees of fading and the method of assessment should be the same as for daylight.

If all fading lamps behaved similarly and there were no controllable operating conditions which might affect light fastness, then nothing more would really be necessary. However, this is not the case, as there is little doubt that the differences in assessment which occur in some cases between various lamps are at least as great as the differences between any one lamp and daylight.

As a daylight test similar to *B.S.*1006 : 1953 had been accepted by the International Organisation for Standardisation, the F.T.C.C. felt that an investigation into the use of fading lamps should be started, especially as the A.A.T.C.C. proposal that its fading lamp method should be accepted internationally had been rejected by the European delegates. The Light Fastness Subcommittee therefore accepted the responsibility for undertaking this investigation, which will undoubtedly take many months to complete. This paper reviews the relevant literature, and discusses the theoretical implications of the suggested causes of anomalies.

It is generally accepted that in many cases fading lamps do give results which are significantly different from those obtained by daylight exposure. Morton[1], for example, tested 289 samples in a fading lamp and by exposure to daylight and found that in nearly half the cases the difference was more than 1 grade. (It must always be remembered that the 1–8 *B.S.* 1006 scale is geometric, and a difference of one grade means that the pattern is twice (or half) as fast in daylight as in a fading lamp.) The only possible reasons for the difference are as follows—

(1) Spectral composition of the incident light
(2) Differences in temperature during exposure
(3) Differences in moisture content during exposure.

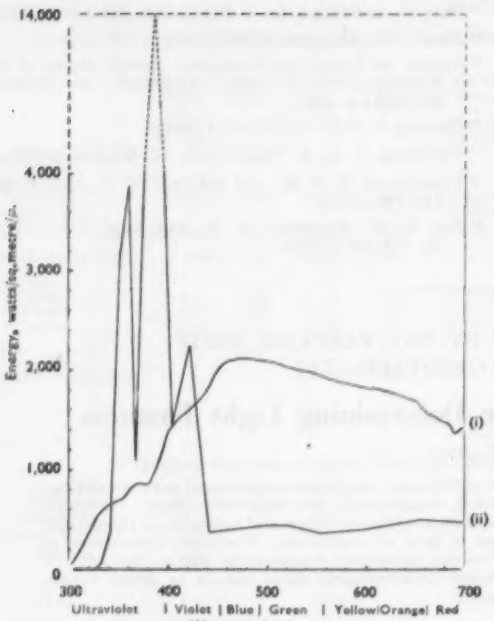
These will therefore be considered in detail, and the theoretical implications of each worked out.

SPECTRAL COMPOSITION OF LIGHT

Although fading lamps employing xenon arcs, mercury-vapour lamps, and filament lamps have been marketed on the Continent, the only artificial light source used to any extent in this country is the enclosed carbon arc. The spectral energy distribution curve of such an arc is shown in Fig. 1 together with the maximum possible curve for daylight (sunlight+skylight) at sea level[2]. It is expected that the curve for average British daylight would be similar in shape, but much lower, the intensity of daylight on overcast days being only about one-fifth of that of clear days[3].

The data for the enclosed carbon arc have been kindly supplied by the Atlas Electric Devices Co., of Chicago, U.S.A., and refer to the energy distribution at the sample position (10 in. from the arc) in the FDA-R Fade-Ometer. It should be pointed out that this arc operates at 2 kw., whereas the majority of lamps in this country operate at only 1 kw., so that the intensity of radiation will be much lower.

The difference in spectral emission between the enclosed carbon arc and daylight is that the former



(i) Sunlight + skylight (maximum)
(ii) Enclosed carbon arc (2 kw.)

FIG. 1

is very much richer in near ultraviolet radiation and deficient in visible radiation in the blue–red region of the spectrum. The enhancement in the near ultraviolet is due to two of the peaks of the cyanogen radical— at 357·5 and 385 mμ.— the intensity at 385 mμ. being fourteen times as great as the maximum possible in daylight. In the blue–red region the intensity in the lamp is only one-fifth of that of the brightest daylight.

Although at first sight it would appear that these differences could cause anomalous fading, it is instructive to consider in detail exactly how.

The greatest discrepancy (due to differences in spectral composition alone) between a fading-lamp and a daylight assessment would occur when the pattern is faded only by ultraviolet radiation and the standards only by visible light, or *vice versa*. Unfortunately, however, very little is known concerning which wavelengths do cause fading: Morton [1], for example, states that "most dyes fade by the action of a comparatively narrow band of wavelengths near the absorption maximum of the dye. Contrary to widely held belief, dye fading is thus due to the visible light and not to the ultraviolet content of sunlight". Appel and Smith [4], however, concluded that the colour of a compound was not a safe guide to the spectral region which causes fading; Blaisdell [5] and Cooper [6] have also published evidence to the contrary.

This lack of precise information undoubtedly arises from the extreme difficulties involved if the problem is approached from a fundamental viewpoint. As Dr. D. A. Clibbens, of the Shirley Institute, has remarked: "Although the fundamental scientist may begin by thinking about the behaviour of dyed textiles exposed to air and daylight, he will probably conclude by working with materials that are not textile materials, that are not dyes, of which air is not an important environment, and that are illuminated by some source of light other than the sun".

Consequently, at present, the only certain conclusion one can make is that which arises from the Grotthus–Draper law, namely that wavelengths which are not absorbed cannot cause fading. If, therefore, there are patterns which reflect strongly in the far violet–near ultraviolet region of the spectrum, marked differences would be expected between fading lamps and daylight if the standards absorbed strongly in this region, or *vice versa*. Lead [7], however, states that: "there are no dyes which reflect at all strongly in the blue and immediate ultraviolet regions. All dyeings, even quite bright blues, absorb quite strongly in the region 380–480 mμ., and it is not surprising, therefore, that such dyes should be faded by light in this region of the spectrum, especially in view of the larger amount of energy associated with one quantum of light at this end of the spectrum". Guthrie [8], at the author's request, measured the reflectance of the eight blue light-fastness standards (*B.S.*1006: 1953), and the curves obtained certainly confirm this view, the absorption values at 385 mμ. (the peak carbon arc wavelength) varying between 81 and 95%.

The only possible mechanism whereby large discrepancies between daylight and fading-lamp assessments could arise directly from differences in spectral composition is, therefore, that far violet and near ultraviolet radiation could be absorbed by a coloured textile and yet not contribute significantly to the photochemical degradation of the colouring matter. This does not seem to be a likely possibility, and therefore it would appear that differences in spectral composition are not directly the main cause of large discrepancies in light fastness assessments.

This is a somewhat unsatisfactory position, however, in that this conclusion has been reached by theoretical reasoning from a paucity of established facts. The author has therefore started an investigation to find out which regions of the solar spectrum are responsible for fading coloured materials, as such knowledge would enable the importance of differences in spectral distribution to be placed in its proper perspective.

TEMPERATURE

Very little work appears to have been done on the direct effect of temperature on the rate of fading, but it seems to be well established that, other factors being equal, an increase in temperature causes an increase in the rate of fading. Thus Hedges [9] found with a dyeing of 0·5% Soluble Pure Blue on wool that the loss in depth was 75% greater at 50°C. than at 10°C., the regain being 18% in both cases and the time of exposure to a mercury arc in quartz also being the same. Launer [10] found that the increases in reflectance of two calibration papers, exposed for the same time in an atmosphere of 58% R.H., were 72% and 84% greater at 60°C. than at 20°C.

If the increase in fading rate caused by an increase in temperature is of the same order for patterns and standards, then no anomalies would be expected, the effect being merely to shorten the time of exposure, which is obviously desirable.

It may well be, however, that the temperature coefficients are quite different and might cause anomalies, but undoubtedly the main effect on the fading rate is indirect, the temperature affecting the moisture content of the material being exposed and the latter affecting the rate of fading. For this reason, rather than its direct effect, the temperature during exposure is of particular interest.

The temperature of a pattern depends on two factors: firstly, it will start by having the same temperature as the surrounding air (providing this is stable enough for equilibrium to be reached), the temperature of this air being measured by a thermometer shielded from the direct rays of the light source; secondly, a pattern exposed to a light source will absorb radiant energy, and all that which is not used photochemically will be converted to heat and will thus raise the temperature of the pattern above that of the surrounding air.

As textile materials are generally poor conductors of heat, there will often be a pronounced temperature gradient between the exposed face of the pattern and the back, but it is only the surface temperature which is important in fading.

Nordhammar [11] measured the surface temperature of black and white wool samples under various conditions (Table I). In all cases, he found the surface temperature of the white sample to be some 18°F. lower than that of the black.

Table I [11]

Position	Max. Surface Temp. of Black Pattern (°F.)
Out-of-doors, in Gothenburg, facing sun, clear summer day, no breeze, air temp. 81°F.	154
As above, but with very light breeze ...	145
Indoors behind a window	140
Behind glass in a fading house	104

In an FDA–R Fade-Ometer (which is recommended by the A.A.T.C.C.), he found the mean surface temperature of the black pattern to be 194°F., rising to 212°F. during short intervals, and the white pattern was only about 5°F. cooler, the shielded air temperature being 131°F. The similarity between black and white patterns in the Fade-Ometer is explained by Nordhammar as being due to the similarity between their reflectance curves in the infrared. The spectrum of the enclosed carbon arc is richer in infrared radiation than sunlight, and thus the differences between the temperatures of black and white are minimised.

Scorching of materials can obviously cause anomalous results but rarely occurs with established fibres such as wool and acetate rayon even in lamps which do not contain a water screen; this problem is, however, acute with some of the newer synthetic fibres. Thus du Pont [12] have stated that "cuprous-ion-dyed Orlon is sufficiently heat-sensitive to be scorched by the excessive heat of some Fadeometers"; the A.A.T.C.C. Light Fastness Committee are studying this problem [13]. The water screen incorporated in all except the earliest British lamps undoubtedly prevents scorching of even the most heat-sensitive materials.

Moisture Content

The surface moisture content of a pattern is possibly the most important single factor affecting the rate of fading and is probably the only one which can account for major discrepancies (2 or more grades) between daylight and fading-lamp assessments.

An increase in the moisture content almost inevitably causes an increase in the rate of fading, other factors being constant, and this effect has been known for many years. Hedges [9] in 1928 measured the rate of fading of fifteen dyes on wool, cotton, or silk, and found a linear relationship between rate of fading and moisture content; in one case the rate of fading was as much as seven times greater at 27·4% moisture content than at 5%. Cunliffe [14], during the original search for light fastness standards, determined the sensitivity to changes in relative humidity of a large number of dyes on cotton, linen, viscose rayon, wool, and silk and divided them into four main classes—of small, moderate, large, and very large sensitivity—the criterion of moderate sensitivity being that the rate of fading at 100% R.H. was twice that at 32% R.H.; the light fastness standards selected all fell in the "small" category.

Anomalies in light fastness results due to differences in moisture content during exposure will therefore occur when the sensitivity to moisture content of the pattern is significantly greater (or possibly less) than that of the standards.

We must therefore consider the probable moisture contents which will occur during exposure to daylight and in a fading lamp.

Daylight Exposures

Daylight exposures are made by exposing pattern and standards "under window glass facing due south and sloping at an angle of 45°; adequate ventilation shall be provided" (*B.S.*1006: 1953). The moisture content during exposure will be governed primarily by the relative humidity of the atmosphere, and in England exposures are often restricted to the relatively sunny months April to October, particularly in industrial districts, where during the winter months fading is very slow but soiling and atmospheric degradation are very high. Assuming that the average relative humidity during the sunny months is 70% and the average temperature 57°F., wool materials will have a moisture content of about 18% if the exposure cabinets are sufficiently well ventilated for the air within to be at the same temperature as the outside air. However, there is little doubt that many exposure frames behave like greenhouses, the large windows admitting infrared radiation, which heats up the inside air, the amount of ventilation provided being insufficient to prevent this.

If the outside air is heated up from, say, 68°F. to 130°F. just under the glass, the relative humidity will drop from 65% to 10% and the moisture content of the pattern will fall from 16% to about

4%. As we have already seen, the surface of the pattern will be hotter than the surrounding air when the sun is shining, and therefore the effective moisture content will be lower still. One might therefore expect that, where there is a marked difference in sensitivity to humidity between pattern and standards, the results of daylight exposures will show variations according to the atmospheric conditions. If the pattern is very much more sensitive than the standards, the result obtained for an exposure made when there was little sun would be expected to be several grades lower than one made when there was continual sunshine. Fortunately, in England these extremes are never likely to occur, for two reasons—firstly, the daylight exposures are usually long enough for considerable differences in weather conditions to occur; and secondly, the fact that the patterns are exposed at night as well as during the day means that the moisture content may be very high during the early morning and the late evening.

Fading-lamp Exposures

Although fading lamps generally employ the same light source, namely the enclosed carbon arc, they differ considerably in the methods adopted to humidify the air in the exposure chamber. Three different types exist—(*a*) dry, (*b*) humidified, and (*c*) screened and humidified—and these vary considerably in the resulting surface moisture content of patterns during exposure.

(*a*) Dry Lamps consist of an enclosed carbon arc and occasionally contain fans, which reduce the temperature inside the exposure chamber. The air temperature at the pattern position in such lamps is usually between 80° and 110°F., but the surface temperature of the pattern will undoubtedly be much higher, as the carbon arc emits a considerable amount of infrared radiation—75% of the total radiation is in the region above 1400 mμ. compared with only 30% for sunlight [15]. Moreover, a significant amount of this radiation is of wavelengths greater than 2200 mμ., which are not present in solar radiation. The surface moisture content of patterns exposed in such lamps will therefore be very low indeed.

(*b*) Humidified Lamps contain some provision for humidifying the air inside the exposure chamber, usually by employing a series of wet wicks; the A.A.T.C.C.-recommended lamps are of this type. The effectiveness of such a system is, however, very low: Nordhammar [11] and Boulton and Guthrie [16] found that the relative humidity of the air round the pattern was only 10%, which corresponds to a moisture content of 4–5% for wool. As the surface temperature of the pattern will be higher than that of the surrounding air, the surface moisture content will be lower still, and it is probable that even with patterns very sensitive to differences in humidity, this type of humidified lamp would not give results significantly different from those obtained in a non-humidified lamp; preliminary experiments have confirmed this.

(*c*) Screened and Humidified Lamps differ from the American type in that between the globe of the arc and the pattern there is a double-walled glass vessel through which a stream of water passes, which absorbs strongly in the region above 1400 mμ. The effect of this screen—which seems to be confined to British lamps—is twofold: firstly the air temperature surrounding the pattern is considerably reduced; and secondly the difference between the surface temperature of the pattern and the air temperature is much less. This, therefore, has the effect of increasing the surface moisture content during exposure.

Two types of screened lamps are currently available: in the C.P.A. fading lamp [17] the humidification is effected by a heatable water tray and a fan, and in the new model of the Fugitometer (Kelvin & Hughes) [18] by an atomiser. Screening therefore enables a much greater range of temperatures and relative humidities to be obtained than in the unscreened types. Thus, whereas Boulton and Guthrie [16] and Nordhammar [11] found regains which corresponded to a relative humidity of about 10% in the unscreened American lamps, Lead [7] obtained a figure of about 67% R.H. in a screened British lamp.

CONCLUSIONS

The discrepancies which sometimes occur between daylight and fading-lamp assessments must be due to differences in spectral composition, temperature, or moisture content during exposure, and the available evidence indicates that the third possible cause is probably the most important.

It is obvious that both daylight and fading-lamp exposures should be such that the results reliably indicate the behaviour which will occur during the normal use of the material under test.

The most attractive method of deciding the conditions under which fading lamps should operate will be to select a number of patterns which are sensitive to each of the possible causes of anomalous fading; these will then be exposed under widely different conditions, and those which give the most reliable results will be specified for routine testing.

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COMMUNICATIONS

Some Factors in the Measurement of Affinities of Vat Dyes for Cellulose

R. H. PETERS and J. SIMONS

Isotherms have been obtained for the adsorption of Caledon Red BN and Caledon Red 5G by cuprammonium rayon yarn at 40°C., in the presence of varying concentrations of sodium chloride and sodium hydroxide. It is shown that consistent values for the affinity of these dyes are obtained only when account is taken of the absorption of hydroxyl ions by the fibre. The use of the "equivalent chloride" ion concentration in calculating the affinity is discussed and shown to be satisfactory.

INTRODUCTION

Vat dyes, possibly as a result of their ever increasing use, have in recent years been the subject of several detailed physicochemical studies. The application of this class of dyes is more complicated than that of other classes and involves several steps. For example, Marshall and Peters [1] and Lineken *et al.*[2] have studied their reduction properties; Boulton and Morton [3], Geake [4], and Fowler, Michie, and Vickerstaff [5] their dyeing properties; and Sumner, Vickerstaff, and Waters [6] their behaviour on soaping.

An examination of dyeing properties [4] has shown that vat dyes have much in common with direct cotton dyes. Thus the activation energies of diffusion are similar, being for direct dyes ca. 14 and for vat dyes ca. 12 kcal./mole, and the thermodynamic approach [7] which has been used for direct dyes can be applied successfully to vat dyes. The affinities of this class of dye are of the same order as those of direct dyes.

As has been pointed out by Fowler *et al.*[5], however, equilibrium studies on vat dyes are difficult, since many of the dyes are not stable to prolonged treatment in strongly alkaline solution in the reduced state, and their ready reoxidation necessitates exclusion of air during the dyeing. The complex nature of the normal dyebath, which contains as anions dye, hydroxyl, hydrosulphite and its oxidation products, and in many cases chloride, makes an exact quantitative treatment difficult. In the thermodynamic treatment used by Fowler *et al.*[5], the simplifying assumptions were made that only the dye anion had affinity for the fibre and that all other anions could be replaced by an equivalent quantity of chloride ions. It was felt, in view of the success attending such a treatment, that the problem merited further study, especially in connection with the small but definite affinity of hydroxyl ions. In the work reported here equilibrium studies have been made on (*a*) the absorption of hydroxyl ions by cellulose and (*b*) the absorption of dyes from dyebaths containing dye, hydroxyl, and chloride ions only. The experiments were carried out with Bemberg yarn at 40°C. The results from these experiments have been treated by a modified form of the theory of Peters and Vickerstaff [7], which takes into account the effect of the absorption by the fibre of hydroxyl ions. This modification yields much more consistent values for the calculated affinities.

THEORETICAL

The object of applying thermodynamics to a system is to obtain a relation between the variables which involves the energetics of the system. Thus, for a dye–fibre system at constant temperature, the change $\Delta\mu_D^\circ$ in the standard chemical potential on adsorption, in terms of the activities a_f and a_s of the dye on the fibre and in the dyebath respectively, is given by equation (i)—

$$-\Delta\mu_D^\circ = RT \ln a_f - RT \ln a_s \qquad \text{(i)}$$

The problem then resolves itself into one of deriving suitable expressions for a_f and a_s. Unfortunately, very little is known about the activities of dye ions in solution, so that a_s is usually replaced by the product of the concentrations of the relevant ions; i.e. for a dye of formula Na_zD, a_s is written as $[Na]^z[D]$, where [Na] and [D] are the concentrations of sodium and dye ions. This step involves the assumptions that the dyes are completely dissociated and that the substitution of concentrations for activities does not lead to significant error.

In deducing an expression for a_f, it is necessary to choose a simple model which approximates to the dye–fibre system. The models generally employed are of two types, depending upon whether the fibre is regarded as a solid phase containing a certain number of fixed sites to which the dye can be attached, or as a homogeneous phase of a certain volume in which the dye is evenly distributed.

The first approach, applied to the absorption of dye acid by wool, has been used successfully by Gilbert and Rideal [8] and Lemin and Vickerstaff [9] and has been described in detail by Vickerstaff [10].

For absorption by cellulose the alternative approach has been used by Peters and Vickerstaff [7], who divided the fibre–dyebath system into two phases— aqueous and cellulosic— and calculated the activity of the dye in the fibre in terms of its concentration. It is assumed that the two phases may be regarded as homogeneous and that a Donnan equilibrium may be considered to exist between them, the dye anions being non-diffusing. Their equation for the affinity of the dye of formula Na_zD is—

$$-\Delta\mu_D^\circ = RT \ln \frac{[Na]_f^z[D]_f}{V^{z+1}} - RT \ln [Na]_s^z[D]_s \qquad \text{(ii)}$$

V is the volume of the cellulose phase associated with 1000 g. of fibre, and f and s refer to concentrations of ions in the fibre and aqueous phases respectively.

It has been argued by other workers [11] that the dye may be regarded as adsorbed on fixed sites in cellulose, thereby giving a localised monolayer as in the case of wool, but it is usually agreed that

there are no sites available for the attendant sodium ions, which are treated as homogeneously distributed throughout the cellulose phase. Theories of a more complex nature have been put forward, but as they do not account for the experimental results more fully than that of Peters and Vickerstaff [7], the latter theory has been used in the present work.

In this paper all the concentrations are expressed as gram-ions per litre. This eliminates the need for introducing the volume term V into the equations to convert concentrations from gram-ions per 1000 g. of fibre to gram-ions per litre. Thus equation (ii) becomes—

$$-\Delta\mu_D^\circ = \boldsymbol{RT} \ln [Na]_f^z[D]_f - \boldsymbol{RT} \ln [Na]_s^z[D]_s \quad \text{(iii)}$$

In order to use this equation to calculate $-\Delta\mu_D^\circ$, the sodium ion concentration on the fibre $[Na]_f$ must be known. This is calculated by assuming a Donnan equilibrium between the aqueous and cellulose phases and applying the condition for electrical neutrality to the cellulose phase—

$$[Na]_f[Cl]_f = [Na]_s[Cl]_s \quad \text{(iv)}$$

$$[Na]_f = [Cl]_f + z[D]_f \quad \text{(v)}$$

These equations enable $[Na]_f$ to be determined, so that equation (iii) can be used to calculate affinities. This equation gives a good representation of experimentally determined isotherms [4,7]. In the work of Fowler *et al.*[5] the anions in the vat dyebath were replaced in the theoretical treatment by an equivalent quantity of chloride ions, the bivalent $S_2O_4^{2-}$ ions being replaced by twice the number of Cl^-. This assumption enabled the affinities to be readily calculated. A good criterion as to whether the system is behaving in accordance with this theory is the slope of the graph obtained by plotting $\log [Na]_f^z[D]_f$ against $\log [Na]_s^z[D]_s$. Using the above treatment, lines were obtained with the theoretical slope of unity. However, the use of equations (iii)–(v) results in lines of the theoretical slope only when the caustic soda concentration is constant, as in the experiments carried out by Fowler *et al.*[5]. It has been shown by various authors [12,13] that hydroxyl ions are absorbed to an appreciable extent by cellulose, and this factor must be taken into consideration in the calculation of vat dye affinities. If it is assumed that the affinity of hydroxyl ions is independent of the dye present, then the change in the standard chemical potential associated with the adsorption of these ions is given by an equation similar to (iii), viz.—

$$-\Delta\mu_{NaOH}^\circ = \boldsymbol{RT} \ln [Na]_f[OH]_f - \boldsymbol{RT} \ln [Na]_s[OH]_s \quad \text{(vi)}$$

The presence of these ions will alter the charge conditions in the cellulose phase, and equation (v) must be modified to—

$$[Na]_f = [OH]_f + [Cl]_f + z[D]_f \quad \text{(vii)}$$

Since it has been assumed that hydroxyl and dye ions are adsorbed independently, $\Delta\mu_{NaOH}^\circ$ may be determined from the adsorption of caustic soda alone. From equations (iv), (vi), and (vii) an equation quadratic in $[Na]_f$ can be derived, viz.—

$$[Na]_f = \frac{K[Na]_s[OH]_s}{[Na]_f} + \frac{[Na]_s[Cl]_s}{[Na]_f} + z[D]_f \quad \text{(viii)}$$

where $\boldsymbol{RT} \ln K = -\Delta\mu_{NaOH}^\circ$. The quantity $[Na]_f$ is then given by—

$$[Na]_f = [D]_f\left\{\frac{z}{2} + \left(\frac{z^2}{4} + \frac{[Na]_s([Cl]_s + K[OH]_s)}{[D]_f^2}\right)^{\frac{1}{2}}\right\} \quad \text{(ix)}$$

In the work described here equations (iii) and (ix) have been used to derive $\Delta\mu_D^\circ$ for two dyes in the absence of the complicating sodium hydrosulphite.

A further point has been examined in this paper. In the work of Fowler *et al.*[5] it was assumed as a first approximation that the anions in a normal dyebath can be replaced, in the calculation of $[Na]_f$, by an equivalent concentration of chloride ions. A better approximation is to consider the Donnan equilibrium of both univalent and bivalent ions. Thus, for the bivalent ion Y, equation (iv) becomes—

$$[Na]_f^2[Y]_f = [Na]_s^2[Y]_s \quad \text{(x)}$$

The corresponding condition of electrical neutrality becomes—

$$[Na]_f = z[D]_f + 2[Y]_f + [OH]_f + [Cl]_f \quad \text{(xi)}$$

From equations (iv), (vi), (x), and (xi) an equation, cubic in $[Na]_f$, can be derived—

$$[Na]_f^3 - z[D]_f[Na]_f^2 - [Na]_s([Cl]_s + K[OH]_s)[Na]_f - 2[Na]_s^2[Y]_s = 0 \quad \text{(xii)}$$

Using the above equation, a more accurate evaluation of $[Na]_f$ can be made, and hence the effect of using the more approximate equation [5] can be ascertained.

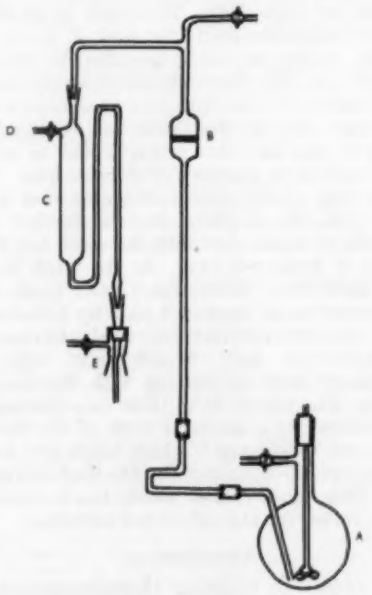

FIG. 1

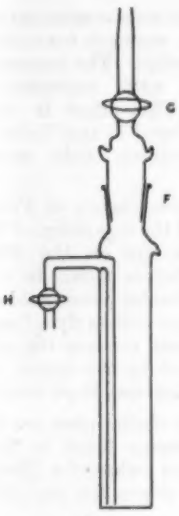

FIG. 2

EXPERIMENTAL

Dyeing Method

The apparatus employed for the reduction of the dyes is shown in Fig. 1. Initially, all the air was swept out of the apparatus with nitrogen, and 500 ml. of a boiled-out solution of caustic soda and sodium chloride was introduced into the litre flask *A*. The dye (0·5 g.) and palladinised asbestos (ca. 0·25 g.) were added, and a stream of nitrogen was passed through. The suspension was heated to 70–80°C. on an electric mantle and stirred vigorously, and a stream of hydrogen was passed through until reduction appeared to be complete, as judged by the colour. The resulting leuco solution was blown by nitrogen, through the sintered glass filter *B* (porosity 1) to remove insoluble material, into the calibrated pipette *C*, tap *D* being open to prevent the liquid from blowing over into the dyeing vessel. Portions of the leuco solution were blown into the dyeing vessel as required.

The dyeing vessel (Fig. 2) consisted essentially of a tube of approx. 150 ml. capacity, which could be sealed (to exclude air during dyeing) by means of taps. For dyeing, a hank of Bemberg yarn (ca. 0·5 g.) was introduced into the dyeing vessel through the ground joint *F* (Fig. 2) together with a solution of caustic soda and sodium chloride, the volume and concentrations of which depended upon the final dye and electrolyte concentrations required. The whole was then boiled to remove dissolved and occluded air, and cooled in an atmosphere of nitrogen. The dyeing vessel was attached to the reduction apparatus through the joint *E* (Fig. 1), and the requisite amount of dye solution blown over from the pipette *C* through *G* (Fig. 2) to give a total volume of 100 ml. All outlet taps were connected to the atmosphere through a trap to prevent diffusion of air into the apparatus. Tap *G* was of wide bore, to allow the solution to pass freely. When the dye vessel was filled, taps *G* and *H* were shut and the vessel was transferred to a thermostat.

Dyeings were carried out at 40°C. for 18 hr., preliminary experiments having shown that this time was adequate for equilibrium to be reached. Geake [4] found that equilibrium is reached in about 4 hr. at 25°C.

The concentration of dye in the dyebath was determined by blowing a fixed quantity of the liquor into a solution of Cellosolve, caustic soda, and sodium hydrosulphite, diluting to a suitable concentration, and estimating colorimetrically by means of a Uvispek (Hilger & Watts) spectrophotometer.

To determine the dye fixed on the fibre, the latter was taken out of the dye vessel, and excess liquor removed with filter paper. The fibre was weighed in a weighing bottle, so that the quantity of loose liquor held could be determined. The fibre together with its entrained liquor was extracted with a solution containing 10 g. sodium hydrosulphite, 180 ml. N. sodium hydroxide solution, and 500 ml. Cellosolve per litre. The resulting dye solutions were estimated spectrophotometrically.

Caustic Soda Isotherms

Five-gram hanks of Bemberg yarn were placed in 250-ml. stoppered conical flasks together with 100 ml. of caustic soda solution of the required strength. The flasks were swept out with nitrogen, and placed in a thermostat at 40°C. for 2 hr. It had been confirmed in earlier experiments that equilibrium was reached in this time. The fibre was removed, and the solution analysed for caustic soda by titration with standard hydrochloric acid.

Materials

The fibre used was Bemberg (cuprammonium rayon) yarn of 120 denier. The yarn was scoured in a solution containing 1 ml. ammonia (sp. gr. 0·880) and 3 g. pure soap per litre for 30 min. at 60°C., washed free from soap, conditioned, and weighed at 65% R.H. At this humidity the moisture content of the yarn was taken to be 11·7%.

Sodium hydroxide and sodium chloride were of analytical reagent quality and the sodium hydrosulphite used was fresh.

The dyes were batch paste samples. The nitrogen and hydrogen were oxygen-free. All joints and taps were greased with silicone grease.

The palladinised asbestos used for catalytic reduction was prepared by the method of Zelinsky and Turova-Pollak [14].

RESULTS AND DISCUSSION

In Tables I and II are given the results for the series of experiments carried out in this work. The data are expressed in gram-molecules or gram-ions per litre for both fibre and solution, the volume of the fibre phase being taken as 0·65 litre per kilogram of fibre. The value of z, the charge on the dye anion, has been taken as two for both dyes.

In calculating the sodium ion concentrations in the fibre phase, the value of K, the equilibrium

constant in equation (ix), has been deduced from the caustic soda isotherm—

$$K = e^{-\Delta\mu^{\circ}_{NaOH}/RT} = \frac{[Na]_f[OH]_f}{[Na]_s[OH]_s} = \frac{[NaOH]_f^2}{[NaOH]_s^2} \quad \text{(xiii)}$$

Thus K is simply the square of the gradient of the isotherm (Fig. 3), and has a value of 10. No attempt has been made to take into account the effect on the $[Na]_f$ term of carboxyl groups on the fibre. The latter, in the case of Bemberg yarn, may amount to 0·015 mole per kilogram of fibre, and would make the true value of $[Na]_f$ smaller than the quoted values. This correction, however, would be insignificant over the range of caustic soda concentrations employed in this work.

Since it has been shown by Fowler *et al.*[5] that the normal $[D]_f$ *versus* $[D]_s$ isotherms for vat dyes are similar to those for direct dyes, it is not considered necessary to reproduce any here. The most interesting new observation is on the effect of increasing caustic soda concentration in a dyebath of constant ionic strength containing caustic soda and sodium chloride. The amount of dye on the fibre decreases with increasing caustic soda concentration. This effect is clearly shown in Table I (Series 4 and 5) and Table II (Series 2–4), in which the caustic soda concentration was varied.

According to the theory of Peters and Vickerstaff[7], the plot of the logarithm of the ionic product $[Na]_f^2[D]_f$ of the dye on the fibre against that of the dye in solution should be a straight line of unit slope. Successful plots of this kind have been obtained for direct cotton dyes[7] and for vat dyes[5] without taking into account the correction for the hydroxyl ion, but in the latter case the caustic soda concentration was kept constant.

In Fig. 4 and 5 similar plots are shown for all the series of experiments listed in Tables I and II, using uncorrected values for $[Na]_f$. The broken lines show the slopes for the different series of

TABLE I

Uptake of Caledon Red BN By Bemberg Yarn

Dye on Fibre (M.)	Dye in Dyebath (M.)	Dyebath Concn. (M.) NaOH	Dyebath Concn. (M.) NaCl	Na^+ on Fibre (M.) Uncorr.	Na^+ on Fibre (M.) Corr.	− Affinity (kcal./mole) Uncorr.	− Affinity (kcal./mole) Corr.
			SERIES 1				
0·284	$6·16 \times 10^{-4}$	0·01	0·20	0·643	0·663	5·21	5·25
0·136	$1·79 \times 10^{-4}$	0·01	0·20	0·388	0·421	4·89	4·99
0·0927	$1·15 \times 10^{-4}$	0·01	0·20	0·322	0·361	4·69	4·83
			SERIES 2				
0·385	$6·99 \times 10^{-4}$	0·01	0·40	0·946	0·961	4·98	4·98
0·281	$3·91 \times 10^{-4}$	0·01	0·40	0·777	0·815	4·93	4·95
0·236	$2·74 \times 10^{-4}$	0·01	0·40	0·709	0·746	4·89	4·95
0·191	$1·74 \times 10^{-4}$	0·01	0·40	0·643	0·681	4·92	4·99
0·122	$9·55 \times 10^{-5}$	0·01	0·40	0·550	0·592	4·82	4·90
			SERIES 3				
0·446	$6·21 \times 10^{-4}$	0·01	0·60	1·20	1·23	4·93	4·96
0·353	$4·07 \times 10^{-4}$	0·01	0·60	1·06	1·10	4·89	4·94
0·319	$3·07 \times 10^{-4}$	0·01	0·60	1·01	1·05	4·94	4·99
0·276	$2·36 \times 10^{-4}$	0·01	0·60	0·945	0·987	4·94	4·99
0·195	$1·52 \times 10^{-4}$	0·01	0·60	0·835	0·876	4·84	4·90
0·136	$7·33 \times 10^{-5}$	0·01	0·60	0·623	0·805	4·71	5·03
			SERIES 4				
0·196	$1·55 \times 10^{-4}$	0·01	0·39	0·641	0·681	5·03	5·25
0·174	$1·55 \times 10^{-4}$	0·02	0·38	0·611	0·685	4·90	5·29
0·170	$2·76 \times 10^{-4}$	0·10	0·30	0·605	0·910	4·51	5·02
0·140	$3·06 \times 10^{-4}$	0·15	0·25	0·565	0·990	4·24	4·94
0·151	$3·04 \times 10^{-4}$	0·20	0·20	0·579	1·10	4·32	5·12
			SERIES 5				
0·0690	$7·16 \times 10^{-5}$	0·05	0·35	0·476	0·655	4·49	4·89
0·0514	$6·62 \times 10^{-5}$	0·10	0·30	0·455	0·774	4·30	4·96
0·0563	$1·28 \times 10^{-4}$	0·15	0·25	0·460	0·896	3·97	4·79
0·0465	$1·86 \times 10^{-4}$	0·20	0·20	0·450	0·988	3·58	4·56
			SERIES 6				
0·0346	$7·01 \times 10^{-5}$	0·10	0·10	0·238	0·505	4·08	5·01
0·0816	$1·89 \times 10^{-4}$	0·10	0·10	0·298	0·559	4·27	5·05
0·0903	$2·26 \times 10^{-4}$	0·10	0·10	0·310	0·568	4·07	5·03
0·1194	$3·27 \times 10^{-4}$	0·10	0·10	0·352	0·605	4·29	5·05
0·1309	$4·73 \times 10^{-4}$	0·10	0·10	0·370	0·618	4·26	4·91
					Mean affinity ...	4·60 (±0·40)	4·98 (±0·14)

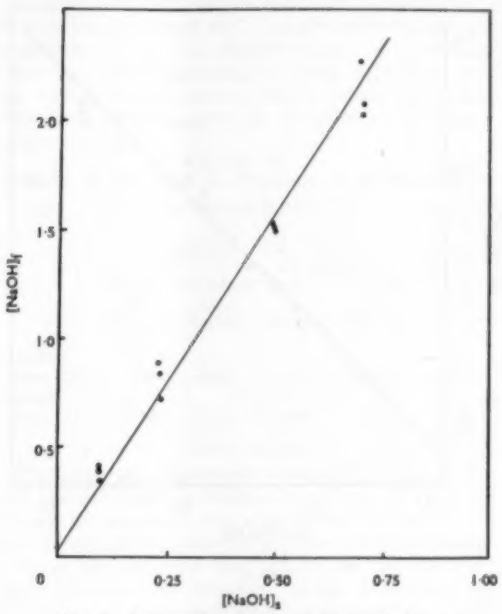

FIG. 3— Isotherm for Absorption of Caustic Soda by Bemberg Yarn

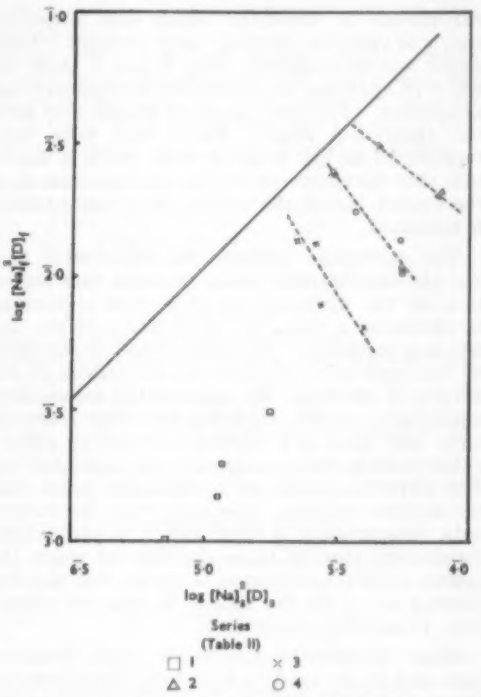

FIG. 5— Absorption of Caledon Red 5G by Bemberg Yarn (Uncorrected Values)

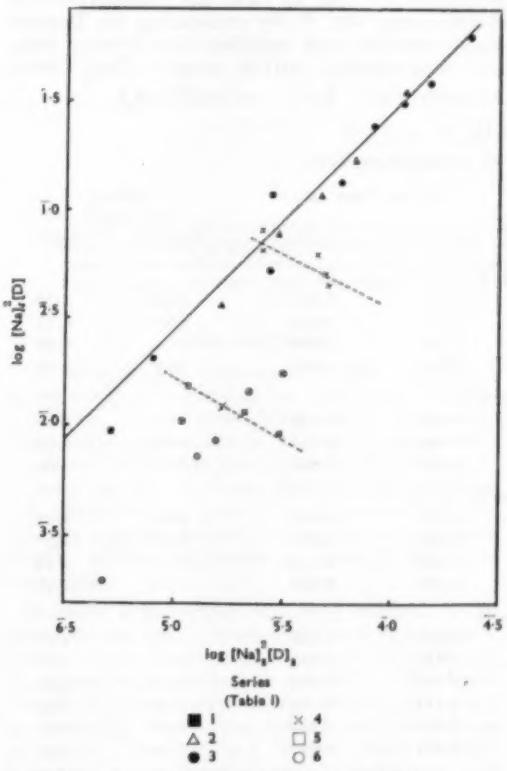

FIG. 4— Absorption of Caledon Red BN by Bemberg Yarn (Uncorrected Values)

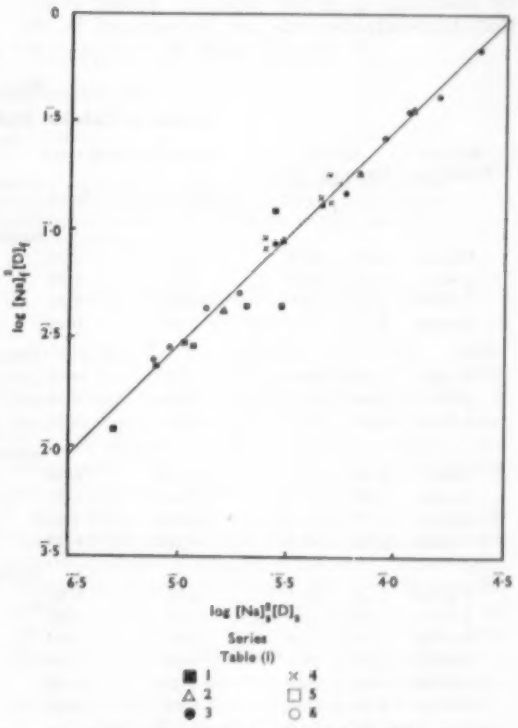

FIG. 6— Absorption of Caledon Red BN by Bemberg Yarn (Values corrected for Hydroxyl Ion Affinity)

experiments in which the caustic soda concentration was varied at constant ionic strength. These slopes are all negative. Fig. 6 and 7 show the effect of applying the correction for hydroxyl ion adsorption. The lines on these graphs now have the theoretical slope. These lines have been reproduced on Fig. 4 and 5, from which it can be seen that the uncorrected points deviate more from the correct line as the caustic soda concentration is increased.

The agreement between the theoretical lines and the experimental points indicates that correction for the hydroxyl ion adsorption is essential in obtaining a value for the affinity of the dye which is consistent. In Tables I and II the effect of this correction is shown in the values of the affinity of the dye. The uncorrected values show appreciably greater variation than the corrected ones, and there is a marked decrease in affinity values with increase in caustic soda concentration. The corrected values are significantly larger than the uncorrected ones, especially where the caustic soda concentration is high; and it is particularly satisfactory that, in those experiments where the caustic soda concentration is varied, the steadily varying values for the affinity become, on correction, remarkably constant.

Some additional experiments with Bemberg yarn and these two dyes have been carried out by Peters and Sumner[15], and in these sodium hydrosulphite has been used as the reducing agent. The results (Table III) have been treated—(*a*) by assuming, as in the paper by Fowler *et al.*[5], that hydrosulphite ions can be replaced in the calculation of $[Na]_f$ by twice the concentration of chloride ions; and (*b*) by considering the Donnan equilibrium for both univalent and bivalent ions, and using equation (xii) to compute $[Na]_f$. Since

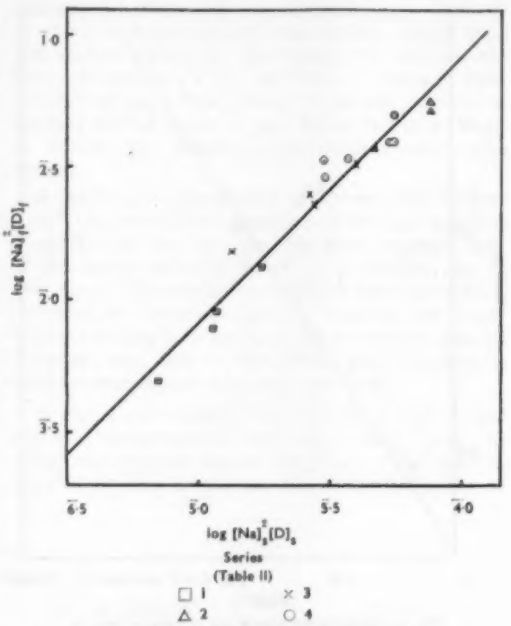

FIG. 7—Absorption of Caledon Red 5G by Bemberg Yarn (Values corrected for Hydroxyl Ion Affinity)

TABLE II

Uptake of Caledon Red 5G by Bemberg Yarn

Dye on Fibre (M.)	Dye in Dyebath (M.)	Dyebath Concn. (M.) NaOH	Dyebath Concn. (M.) NaCl	Na^+ on Fibre (M.) Uncorr.	Na^+ on Fibre (M.) Corr.	− Affinity (kcal./mole) Uncorr.	− Affinity (kcal./mole) Corr.
			SERIES 1				
0·0485	$4·42 \times 10^{-4}$	0·10	0·10	0·255	0·523	3·22	4·12
0·0352	$2·89 \times 10^{-4}$	0·10	0·10	0·238	0·506	3·20	4·14
0·0309	$2·82 \times 10^{-4}$	0·10	0·10	0·233	0·500	3·14	4·06
0·0206	$1·77 \times 10^{-4}$	0·10	0·10	0·222	0·491	3·09	4·08
			SERIES 2				
0·113	$2·89 \times 10^{-4}$	0·01	0·39	0·529	0·569	4·06	4·15
0·0840	$4·69 \times 10^{-4}$	0·10	0·30	0·494	0·811	3·49	4·10
0·0723	$4·80 \times 10^{-4}$	0·15	0·25	0·480	0·849	3·35	4·06
			SERIES 3				
0·0647	$8·54 \times 10^{-5}$	0·005	0·39	0·465	0·484	4·01	4·38
0·0630	$1·67 \times 10^{-4}$	0·045	0·35	0·463	0·629	3·89	4·27
0·0415	$1·77 \times 10^{-4}$	0·095	0·30	0·438	0·746	3·52	4·19
0·0351	$2·55 \times 10^{-4}$	0·195	0·20	0·432	0·960	3·18	4·17
			SERIES 4				
0·0958	$1·90 \times 10^{-4}$	0·01	0·39	0·509	0·549	4·17	4·27
0·0960	$1·87 \times 10^{-4}$	0·02	0·38	0·510	0·592	4·18	4·37
0·0766	$2·28 \times 10^{-4}$	0·05	0·35	0·485	0·665	3·86	4·25
0·0622	$3·36 \times 10^{-4}$	0·10	0·30	0·473	0·788	3·46	4·09
0·0525	$3·43 \times 10^{-4}$	0·15	0·25	0·457	0·859	3·30	4·08
0·0505	$3·45 \times 10^{-4}$	0·20	0·20	0·454	0·991	3·26	4·23
				Mean affinity ...		3·55 (±0·38)	4·18 (±0·10)

the agreement with the present work is reasonable, it may be concluded that the presence of sodium hydrosulphite is no disadvantage in assessing affinities. A comparison of $[Na]_f$ calculated by the two methods shows only a small difference with no significant effect on the calculated affinity values.

TABLE III

Affinity of Vat Dyes in Presence of Hydrosulphite

Dye	Peters and Sumner [15]				Present Work
	$[Na]_f$		−Affinity (kcal./mole)		−Affinity (kcal./mole)
	Equiv. Cl^- Method	Bivalent Ions Method	Equiv. Cl^- Method	Bivalent Ions Method	
Caledon Red BN	1·34	1·32	4·71	4·68	4·98
Caledon Red 5G	1·22	1·20	4·29	4·27	4·18

CONCLUSIONS

The experimental results obtained in this work, and the calculations made, show that, in order to obtain an accurate and consistent evaluation of the affinity of vat dyes for cellulose, it is necessary to take into account the affinity for the fibre of the hydroxyl ions present. If the adsorption of the dye and hydroxyl ions is assumed to occur independently, a correction may be introduced, and the affinities calculated on this basis show good agreement with those obtained from experiments in which sodium hydrosulphite was used as the reducing agent.

Hence the method of Fowler *et al.*[5], which involves the assumption that all anions may be replaced by an equivalent concentration of chloride ions, is quite satisfactory when the affinity of the hydroxyl ions for cellulose is taken into account.

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Qualitative and Quantitative Analysis of Vat Dyes by Paper Chromatography

ERWIN KLINGSBERG

By operating in a nitrogen atmosphere, it has been found possible to effect chromatographic separations of vat dyes in leuco form on strips of paper or synthetic fibres. The technique has been applied to the quantitative analysis of model mixtures, employing spectrophotometric determination of the individual constituents after their chromatographic isolation from the mixture.

INTRODUCTION

Chromatographic techniques, though very useful in the study of water-soluble dyes (such as acid, metallised, and direct dyes), have apparently found little application to vat dyes, presumably because of their great insolubility in inert solvents. In view of the notorious difficulty of purifying and characterising this class of compounds by ordinary organic chemical techniques, a chromatographic method applicable to them should have great value.

It seems evident that any such method, to be generally applicable, must operate on the leuco or reduced form, the form in which all vat dyes, by hypothesis, show reasonable solubility. The leuco form is, of course, very readily oxidised, and must be protected from atmospheric oxygen to be preserved. Bradley and Waller have recently described paper-chromatographic separations of certain anthanthrone derivatives in leuco form [1].

QUALITATIVE ASPECTS OF THE PRESENT METHOD

When an alkaline solution of sodium hydrosulphite is allowed to diffuse along a strip of filter paper which has been spotted with a vat dye and suspended in an atmosphere of nitrogen, a degree of colour migration occurs. Certain mixtures can be separated in this way, but for most purposes the rate of migration seems to be too low.

Now these conditions are favourable for the dyeing of the strip by the leuco vat dye, and hence relatively unfavourable for migration. Accordingly, migration should be aided by less favourable dyeing conditions, i.e. conditions of reduced affinity for the strip. Two methods have been found for reducing affinity in the proper degree—

(1) It is well known that synthetic fibres, compared with cellulose, have much lower affinity for vat dyes. When such fabrics are used, instead of paper, in chromatographic experiments, the

dyes move faster and separate better. Sharp separations of vat dye mixtures have been obtained without difficulty on strips of Dacron, in the apparatus to be described. Other synthetics, including nylon and Orlon, also have been found suitable for leuco chromatography.

(2) Rao, Shah, and Venkataraman[2] report the use of a vatting reagent consisting of an aqueous solution of sodium hydrosulphite and (instead of sodium hydroxide) tetraethylenepentamine. By means of this reagent these authors were able to separate vat dye mixtures on a column of powdered cellulose, or on sheets of filter paper by radial diffusion*.

In the present study, this vatting solution[2] proved much superior to caustic alkaline sodium hydrosulphite in effecting separations on paper. Strips of paper are, moreover, easier to manipulate than those of synthetic fibres, and give much deeper and more "normal" shades from the respective dyes, corresponding to the familiar hues on cotton, whereas the shades on synthetic fibres are often different, and of low intensity.

A variety of vat dye mixtures have now been analysed by descending chromatography along a paper strip suspended from a beaker containing sodium hydrosulphite–tetraethylenepentamine solution, the whole being supported in a large upright tube which is evacuated and then filled with nitrogen at the start of the analysis. After isolation on the paper strip, the individual constituents may be identified by reflectance spectrum or, after elution in a suitable solvent, by absorption spectrum.

Paper partition chromatography ordinarily requires two liquid phases, one fixed and the other mobile, while the paper is thought to function principally as an inert support. The present method employs only one liquid phase, but the paper can no longer be considered inert, inasmuch as affinity for cellulose is an essential characteristic of leuco vat dyes. Thus partition occurs between the paper itself as the fixed phase and the hydrosulphite solution as the mobile phase. In any chromatogram, the components are distributed away from the initial spot in order of decreasing affinity for the fibre under the experimental conditions employed. Variations in these conditions may show significant differential effects; for example, the affinity order for synthetic fibres is different from that for paper strips.

Under the experimental conditions described in the present paper, the affinity order of any pair of dyes has been found to be fixed, i.e. unaffected by the presence of other dyes. Consequently it has been possible to arrange a number of representative dyes in an overall order of decreasing affinity (Table I). Any mixture of dyes from the table may be expected to separate in the order shown, each dye displacing all those below it.

The lowest three or four members of the table diffuse relatively rapidly, and can be washed completely off the paper in a few hours or a day. Higher up the table the migration is progressively slower, and dyes at the top of the table may need a week or more for separation.

Separation of any mixture is cleaner and faster when the constituents are not too close to each other in the table. It will be noted (Table II) that the quantitative analyses were performed on mixtures of constituents relatively widely spaced in Table I (though in point of fact it happens that the quantitative work was done first, and the affinity table assembled afterwards). Such mixtures separate readily into isolated zones, as seen in the plate (Fig. 1 and 2). Dyes close to each other in the table tend to separate less rapidly and completely.

Table I shows that the order of affinities, found by the present method, has no correlation with substantivity under dyeing conditions[4]. Present understanding of the affinity phenomenon does not offer any obvious explanation for the disagreement, although the differences in conditions between dyeing and chromatography are obvious. The specific influence of the tetraethylenepentamine was examined by replacing it with sodium hydroxide, in the chromatography of a few representative mixtures from the table. In most (but not all) cases, the affinity order was unaffected: separation (insofar as it occurred) followed the tabular order rather than the substantivities reported under dyeing conditions.

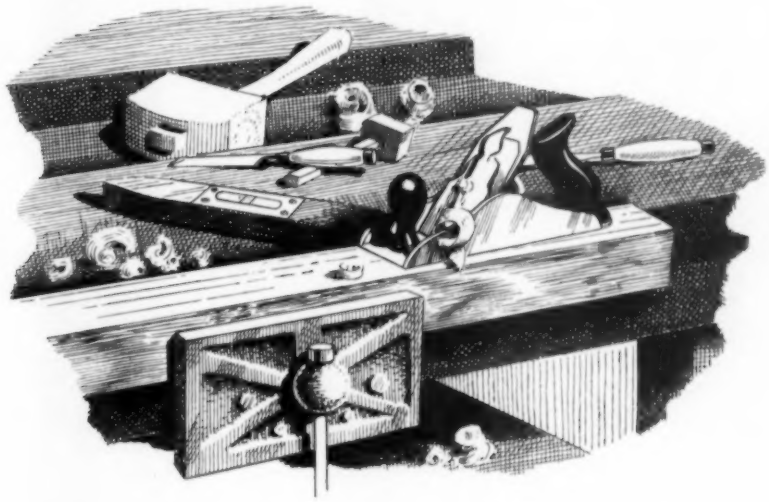
While it is possible to chromatograph leuco vat dyes on columns of powdered cellulose, talc, or other media, paper chromatography offers a number of advantages. It requires very small amounts of dyes and reagents. Once set up, it needs no further attention, but will proceed without danger of interruption by running out of developer, variations in pressure, and the like. Obviously, this feature is particularly desirable in the manipulation of leuco dyes, which must be protected against air oxidation during the extended periods of time that are often necessary for accomplishing clean separations.

Another advantage of paper chromatography is that the finished chromatogram constitutes a conveniently preserved record of the analysis.

With the relatively slow migrations that are characteristic of leuco vat dyes, descending chromatography is much preferable to ascending, for it permits development to be continued almost indefinitely. The ascending technique suffers from the limitation that the process ceases once the strip is wet through; in many cases, development is incomplete at this point.

The radial diffuson technique employed by Rao *et al.*[2] requires a minimum of time, trouble, and apparatus; a sheet of filter paper is sandwiched between two horizontal glass plates, of which the upper has a small hole in the centre, through which the dye sample is introduced, followed by reducing developer solution. Separations are readily and rapidly obtained in this way, but the diffusion across the paper, and the resulting distribution pattern, are rather irregular. Consequently the utility of this method seems to be limited to the qualitative examination of relatively simple

* Midgelow[3] had previously employed a caustic alkaline hydrosulphite solution containing Cellosolve for the chromatographic separation of vat dyes.



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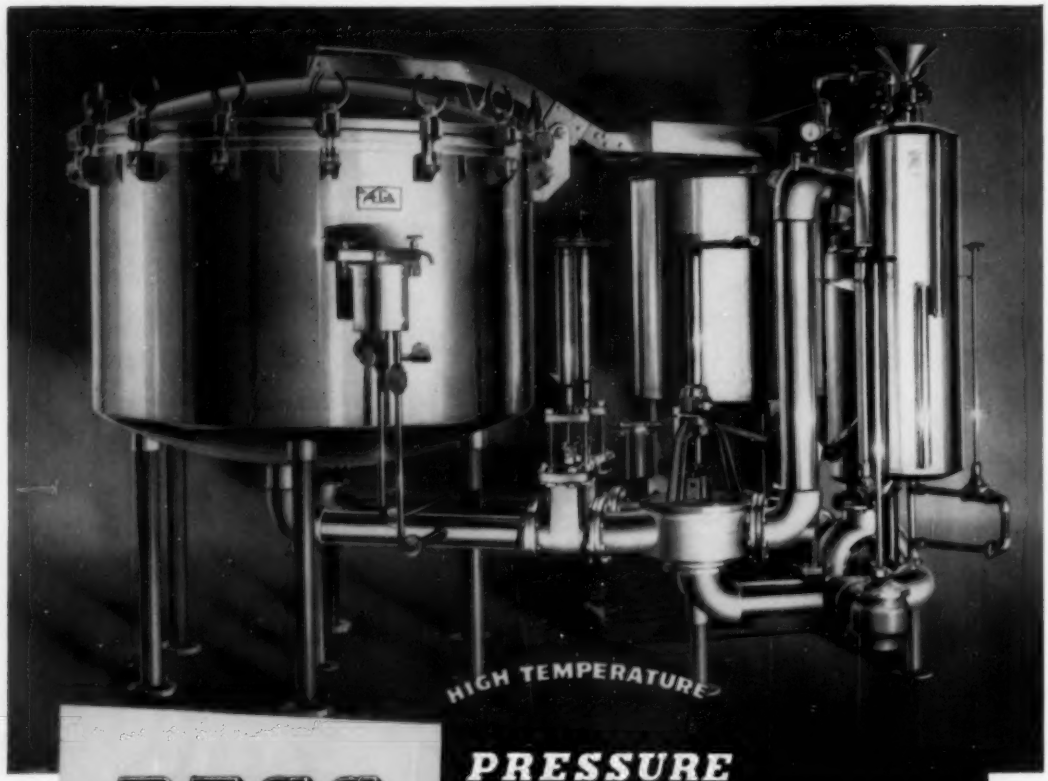

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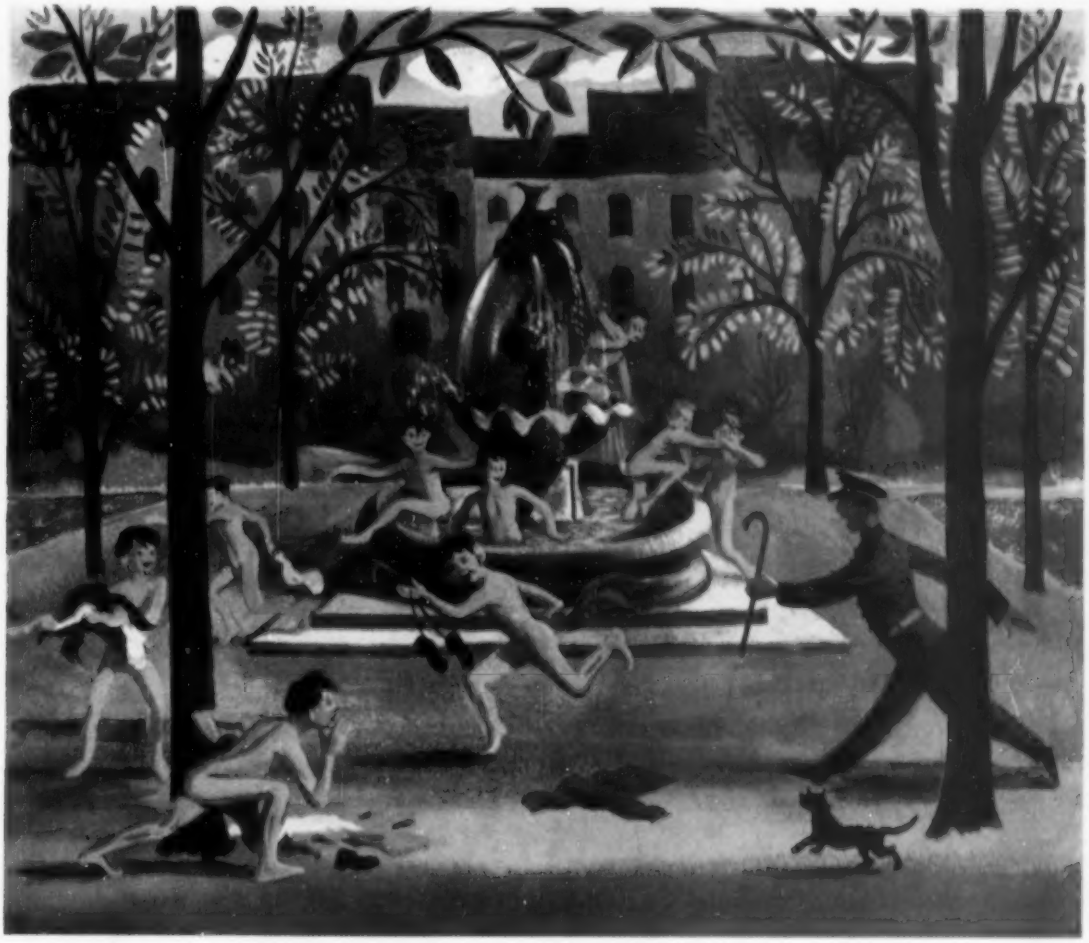

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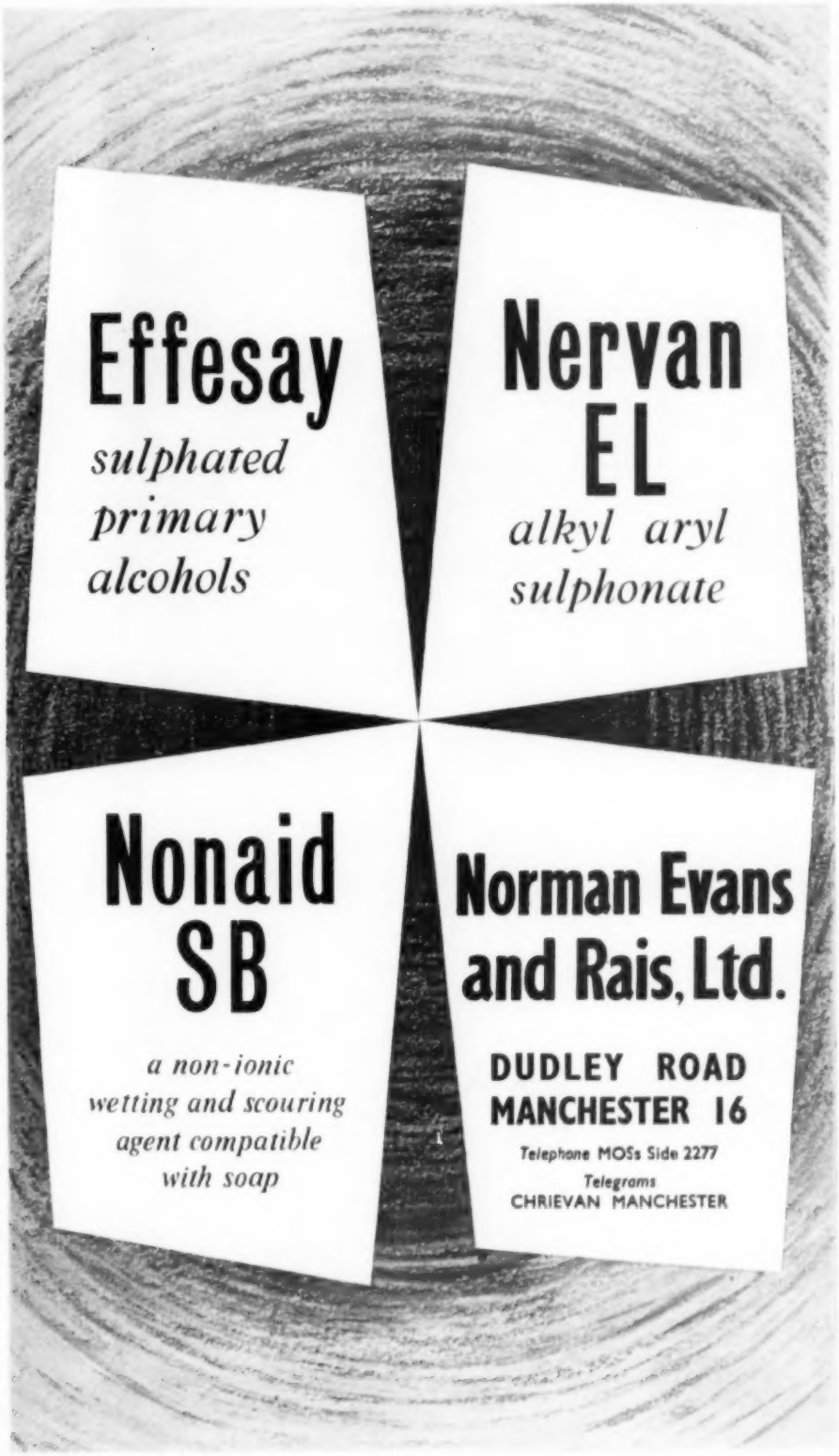
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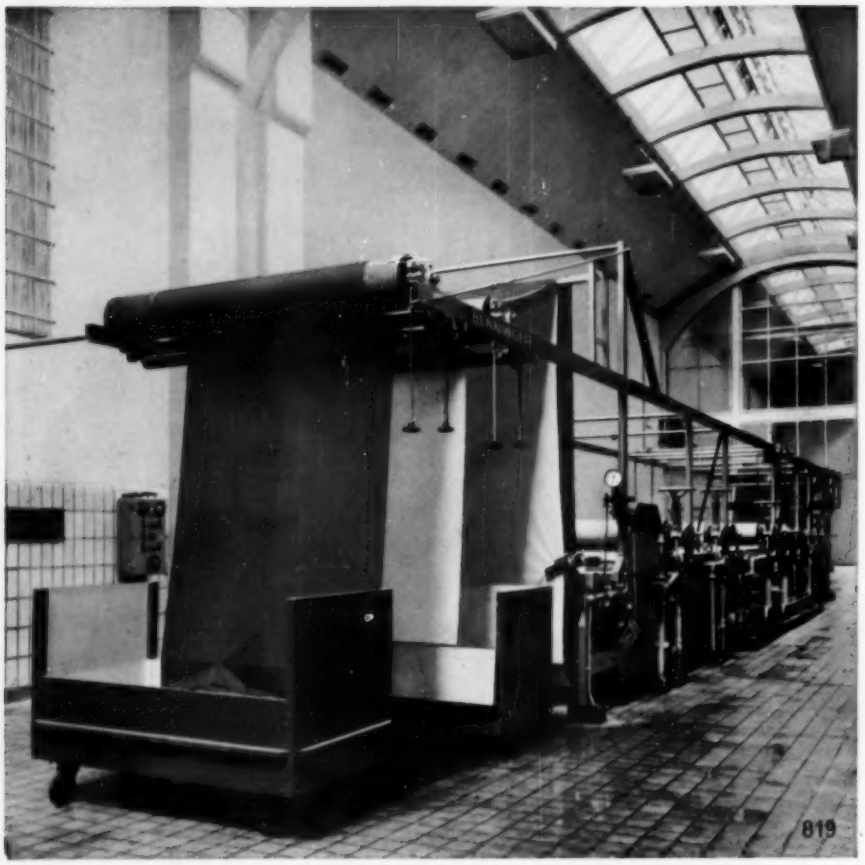

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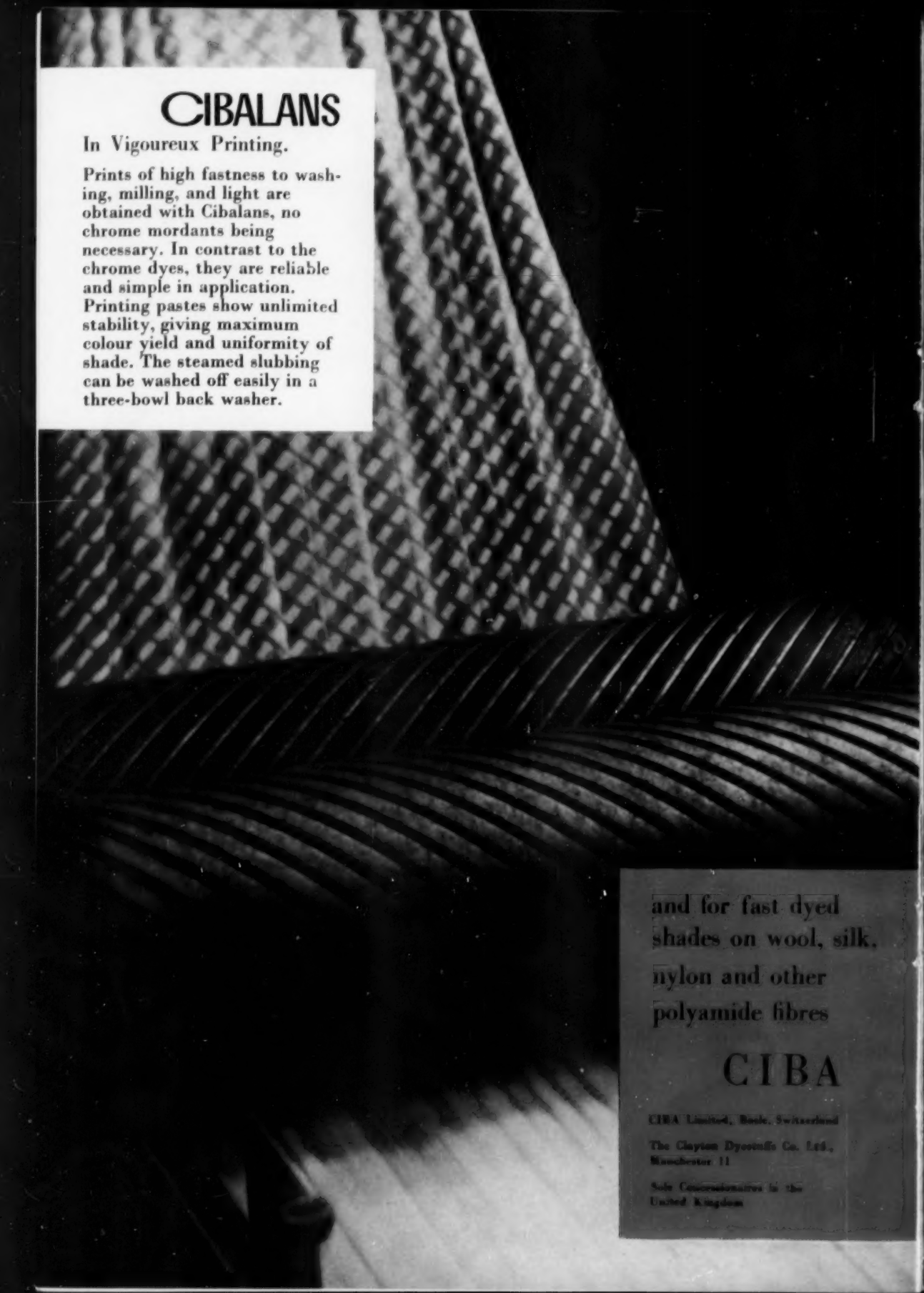

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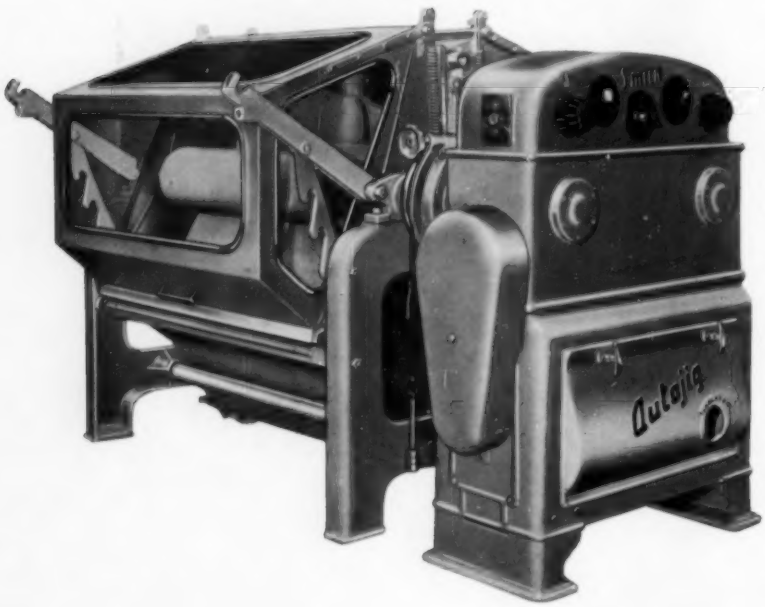

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mixtures of dyes which are conspicuously different in hue; for, without spatial localisation of each component, there is no convenient way of distinguishing it from other components which it may happen to resemble.

QUANTITATIVE ASPECTS OF THE METHOD

When spatial localisation is achieved, as in the present method, it becomes a simple matter, in principle, to carry out a quantitative analysis of a chromatogram by determining each spot. In the present study, this has been accomplished by means of elution in dimethylformamide, followed by spectrophotometric determination of the respective colours against known standards.

Even in dimethylformamide, one of the best inert solvents known for vat dyes, solubilities are limited, but it was found possible to perform satisfactory determinations at concentrations of approx. 2–3 mg./litre. At such concentrations, in a cell 5 cm. deep, the dyes that were determined show transmittances, at their respective absorption peaks, of about 5–50%. The 5-cm. cell employed held 15 ml. of solution, so that it was convenient to elute each spot into 25 ml. of dimethylformamide in a volumetric flask. The desired concentration range of 2–3 mg./litre is then given by spots containing 50–75 μg. of dye. Accurately measured quantities of dye, of this order of magnitude, are readily applied (in leuco form) to paper strips from ultramicro pipettes, and can be chromatographed in the apparatus to be described.

Prepared mixtures of vat dyes were analysed by this technique; the results are summarised in Table II.

EXPERIMENTAL DETAILS

Materials

Tetraethylenepentamine (Carbide & Carbon Chemicals Co.) is a viscous liquid, conveniently kept as a reagent in the form of a 10% aqueous solution (100 c.c. of amine in 1 litre of water).

"Developer solution" was prepared as needed by dissolving 10 g. of sodium hydrosulphite in 100 ml. of the 10% aqueous amine.

For the quantitative experiments, chromatographically homogeneous dye specimens were used: i.e. each gave only one zone when chromatographed alone. They were freed from electrolytes by vatting, filtration of the vat, and reoxidation, followed by filtration, washing, drying, and grinding to 200-mesh.

Dimethylformamide was distilled before use.

Apparatus and Method

The apparatus is shown in Fig. 3. A glass tube, 20 in. long and 2½ in. in diameter*, sealed with a stopcock at one end, is supported in an upright position. Within the tube is placed a support 15 in. long, made by bending each end of a piece of glass rod into a small triangle perpendicular to its own length. Upon this support rests a 50-ml. beaker.

A strip of filter paper (Whatman No. 4), 1½ in. wide and 20–24 in. long, is streaked with the specimen to be analysed, 7 in. from one end. Commercial dye pastes, somewhat diluted, are advantageous because of their high state of dispersion; they are readily applied and reduced on the paper. Alternatively, it is convenient to

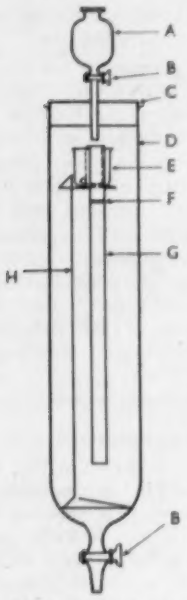
* All dimensions are approximate.

TABLE I

Affinity Order of Representative Vat Dyes

Colour Index No.†	Dye	Class	Substantivity under Dyeing Conditions [4]
969	Hydron Blue	Sulphurised vat	High
—	Vat Olive T	Acridine	Low
—	Vat Red FBB	Oxazole	Low
—	Vat Yellow GC	Thiazole	Medium
—	Vat Olive Green B	Acridine	High
1099	Vat Dark Blue BO	Dibenzanthrone	High
—	Cibanone Red G	Triazine [5]	—
1151	Vat Brown R	Carbazole	Low
—	Indanthrene Brilliant Orange GR	Iminazole [6]	—
—	Indanthrene Bordeaux RR	Iminazole [7]	—
1162	Vat Red BN	Acridone	Low
1118	Vat Yellow G	Flavanthrone	Medium
1101	Vat Jade Green	Dibenzanthrone	High
1096	Vat Golden Orange G	Pyranthrone	Medium
—	Vat Yellow 5GK	Acylaminoanthraquinone	Medium
1135	Vat Brilliant Violet RK	Acylaminoanthraquinone	Low
1131	Vat Red 5GK	Acylaminoanthraquinone	—
—	Vat Golden Yellow GK	Dibenzopyrenequinone	Medium
1207	Vat Red B	Thioindigo	Medium
1177	Indigo	Indigo	Low
1126	Algol Yellow WG	Acylaminoanthraquinone	—
—	Anthraquinone	—	—

† These numbers refer to the First Edition of the *Colour Index*. Structures for the other dyes will be found in the AATCC monograph [4] or the paper by Fox [4–7].



A 60-ml. Dropping funnel
B Stopcock
C Rubber stopper
D Glass tube
E 50-ml. Beaker
F Dye specimen
G Paper strip
H Glass rod support

FIG. 3—Apparatus for Paper Chromatography under Nitrogen

apply the specimen in the leuco form, which reoxidises immediately to give effective dispersion on the paper. A streak about $\frac{1}{8}$ in. wide is usually satisfactory.

The paper strip is then folded into the beaker and placed on the support as shown, the lower end being cut off about 2 in. from the bottom of the tube. A glass weight in the beaker holds the strip firmly in place. The dye specimen is located about 1 in. below the beaker. Preferably, the strip should hang free without touching the wall of the tube, the rod support, or the outside of the beaker. However, this is not always easy to accomplish, and in practice it has been found that results are not impaired by a limited degree of contact.

When the strip is in place, the apparatus is sealed by a rubber stopper holding a 60-ml. dropping funnel, centred over the beaker. Through the bottom stopcock the apparatus is then evacuated and filled with nitrogen. (The nitrogen is conveniently collected and delivered at atmospheric pressure by means of water displacement in gas-washing bottles or similar apparatus.) During the introduction of the nitrogen, about 25–30 ml. of developer solution is drawn into the beaker through the dropping funnel, a few millilitres being retained in the funnel to keep out air.

The apparatus, closed at both ends, is then allowed to stand. Chromatographic development occurs in the usual way, by diffusion of the solution down the strip. The constituents separate into zones which, depending on the nature of the mixture and on the development time allowed, may remain contiguous or (as with the mixtures reported in Table II) may become isolated from each other by areas of colour-free paper. A minimum of 18 hr. is usually required; complex mixtures may take up to a week or more.

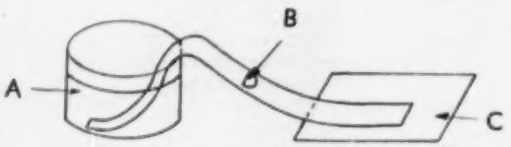
When development appears complete, the appearance of the bands in the leuco state is noted, the apparatus is dismantled, and the strip is oxidised in air, rinsed, and dried.

Preparation of Quantitative Standards

It was found impossible to prepare spectrophotometric standards in dimethylformamide by the obvious method of dissolving a known weight of dye in a known volume of solution. Vat Dark Blue BO, for example, proved very slow to dissolve even at extreme dilution, and decomposed on prolonged refluxing. Consequently the following technique was developed, by which a known weight of dye is spotted on paper and then eluted.

A 10–20 mg. sample of dye is weighed into a 25-ml. volumetric flask and agitated gently with 15–20 ml. of developer solution containing 1·0 ml. of 5 N. sodium hydroxide solution*. After several hours, the solution is diluted to the mark with developer solution and mixed. A clean dry 100-μl. pipette is filled to the mark with the leuco solution, and discharged on the centre of a $1\frac{1}{2}$ in. × 10 in. strip of filter paper. The leuco dye is, of course, rapidly oxidised on exposure to air. The pipette is then rinsed once or twice with dilute sodium hydroxide–sodium hydrosulphite solution, and emptied on to the spot of colour. Cleansing is greatly facilitated if the pipette containing the rinse solution is gently warmed on the hot-plate. The intense colour of the dyes aids inspection of the pipette for completeness of delivery. Before re-use, the pipette is rinsed with distilled water followed by acetone, and dried.

The spot of colour is then cleansed of amine and salts by the method shown in Fig. 4. One end of the strip is folded into a dish containing water, which diffuses along the strip and is removed at the other end by absorption into two or three thicknesses of paper towel. When the towel is

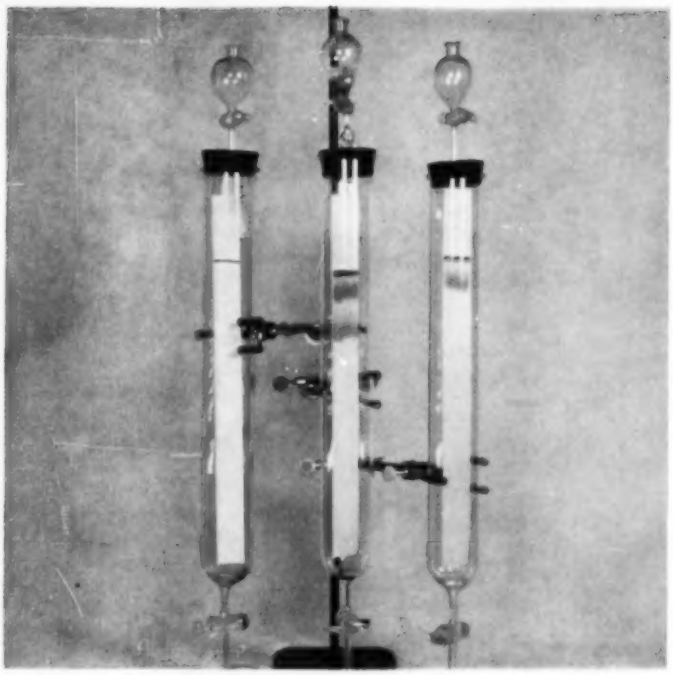


A Water
B Spot
C Paper towel or other absorbent material

FIG. 4—Method of Washing Spots

* The desirability of using tetraethylenepentamine in the standard leuco solutions has not been specifically studied. However, Rao *et al.*[3] report that the amine gives "remarkably stable" vats, and these vats do seem to be relatively slow to oxidise in air. Inasmuch as surface oxidation is a major source of difficulty and error in volumetric work with leuco dye solutions, the presence of the amine may be helpful; it is certainly not harmful.

The sodium hydroxide increases the solubility of the leuco form. It is not necessary with all dyes, but may be added as a routine measure to ensure completeness of solution.



Vat Olive Green B

Vat Jade Green

Vat Golden Yellow GK

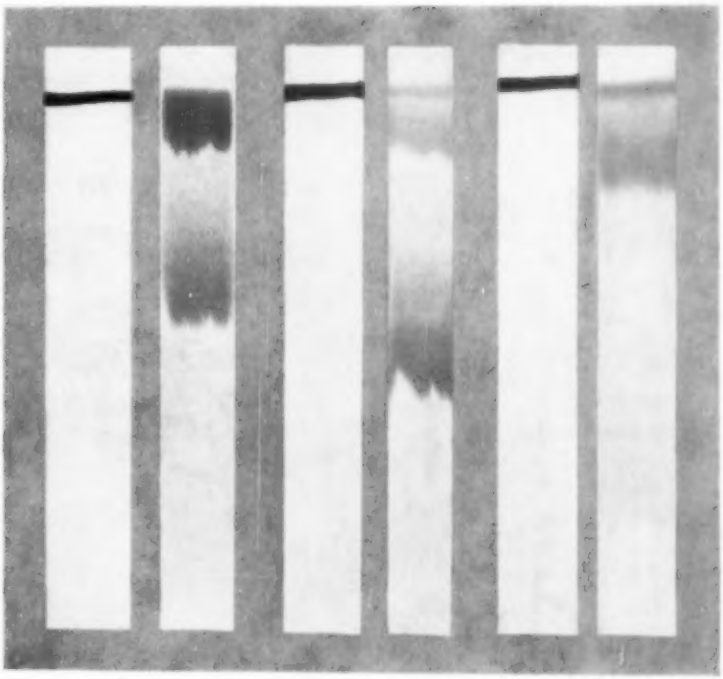
A Original specimen

B Completed chromatogram in leuco state

C Completed and reoxidised chromatogram

A B C

FIG. 1.—Chromatographic Analysis of Mixture of Vat Dyes



A Vat Dark Blue BO
Vat Jade Green
Vat Golden Yellow GK

B Vat Yellow GC
Vat Red BN
Vat Red B

C Vat Red FBB
Vat Brown R
Vat Golden Orange G

A B C

FIG. 2.—Analysis of Representative Mixtures, showing Strips before and after Chromatography

thoroughly wet in an area 2–3 in. across, the strip is removed and dried. Physical contacts with the spot are avoided. Ordinary rinsing is unsuitable because it dislodges traces of colour.

The coloured spot is cut out of the dried strip and placed in about 15 ml. of dimethylformamide in a 50-ml. beaker. Elution seems to be easiest with those dyes which are chromatographically mobile. For example, dimethylformamide readily dissolves spots of Vat Golden Yellow GK at 100°C. and Vat Jade Green at slightly higher temperatures. Vat Dark Blue BO and Vat Olive Green B, on the other hand, which show higher affinity on the strip, are slow to dissolve unless the temperature is raised close to the boiling point. For this purpose, it is convenient to heat the beaker of dimethylformamide (b.p. 153°C.) on the hot-plate in a dish containing bromobenzene (b.p. 156°C.), allowing the maximum temperature attainable without risk of loss by splattering. For the more easily eluted dyes the bromobenzene may be replaced by chlorobenzene or water.

When elution from the paper is complete, the solution is filtered through a plug of cotton wool into a 25-ml. volumetric flask. The paper and beaker are then rinsed into the flask with several 2–3 ml. portions of dimethylformamide. The solution is cooled to room temperature, diluted to the mark, and mixed. It is transferred to a spectrophotometer cell, and the absorption measured in the visual range. Duplicate curves should agree within 1–2%, and will then serve as standards for the determination of the respective dyes after their chromatographic isolation from mixtures. The modified Hardy-type recording spectrophotometer[8], used in the present study, is extremely convenient for the purpose.

Quantitative Analyses

Analyses may be performed in two ways, designated for convenience the "absolute" and the "relative". In the absolute method, a known weight of sample is applied to the strip, and each component determined directly as a percentage of the whole. In the relative method, on the other hand, the sample weight is not known, but all constituents must be determined before any of them can be found as a percentage of the whole.

The following procedure was used for the preparation and analysis of model mixtures by the absolute method. Samples (5–30 mg. each) of the component dyes are weighed together into a 5-ml. volumetric flask, and vatted by gentle agitation for several hours at room temperature with about 3 ml. of developer solution and 0·5 ml. of 5 N. sodium hydroxide solution. Vigorous agitation should be avoided, since it may cause foaming and make it impossible to observe the volume of the solution. When vatting is complete, the mixture is diluted to the mark with developer solution, and mixed. A clean, dry 10-μl. pipette is filled to the mark, and the solution deposited as a fine line across the paper strip in the position previously described. The pipette is then rinsed twice on the specimen with warm dilute sodium hydroxide–sodium hydrosulphite solution. The chromatogram is developed in the usual manner, the apparatus (Fig. 3) being protected from light as much as possible. When development is complete, the stopper and dropping funnel are removed, and the developer solution is withdrawn from the beaker by suction and replaced by distilled water, several rinses being employed. This is done without disturbing the strip; the leuco dyes are rapidly oxidised on the paper. The apparatus is then closed again, and the process of diffusion down and off the strip continued overnight or longer. In this way the amine and salts are removed without disturbing the zones of colour.

TABLE II

Quantitative Analyses

	Mixture	Present (%)	Found (Relative) (%)	Found (Absolute) (%)
1	Vat Dark Blue BO	48·4	49·4	—
	Vat Jade Green ...	51·6	50·6	—
2	Vat Dark Blue BO	70·8	69·8	70·8
	Vat Golden Yellow GK	29·2	30·2	30·6
3	Vat Olive Green B	37·8	37·2	36·2
	Vat Jade Green ...	62·2	62·8	60·9
4	Vat Dark Blue BO	44·0	44·4	46·4
	Vat Jade Green ...	32·0	30·6	31·9
	Vat Golden Yellow GK	24·0	25·0	26·1
5	Vat Olive Green B	34·8	32·6	34·0
	Vat Jade Green ...	22·2	22·1	23·1
	Vat Golden Yellow GK	43·0	45·3	47·4

The strip is then carefully removed and dried at room temperature. The zones are cut out, eluted by the technique used for the standards, and determined by spectrophotometric comparison with the standard absorption curves, taking the measurements at the absorption peak, or at more than one peak if present. The weight of dye in each zone, thus found, is converted directly to a percentage, since the sample weight is known.

For analysis by the relative method, the technique is the same, except that it is not necessary to dilute the leuco mixture exactly to 5 ml. or to apply specimens of exactly 10 μl. to the paper.

Results obtained by both methods are presented in Table II.

* * *

The author wishes to express his gratitude to Mr. F. C. Dexter and his staff for the numerous spectrophotometric analyses performed by them.

AMERICAN CYANAMID CO.
RESEARCH DIVISION
BOUND BROOK N.J.
U.S.A.

(*Received 31st May 1954*)

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Notes

Meetings of Council and Committees November

Council— 10th

Finance— 1st, 10th, and 26th

Publications— 16th

Colour Index Editorial Panel— 26th

Diplomas Executive Subcommittee— 24th

Fastness Tests Co-ordinating— 18th

Abstractors— 5th

Deaths

We regret to report the loss by death of Mr. A. W. Dudbridge and Dr. O. Oberländer, a member of the Society since 1910.

Committee on Methods for the Measurement of the Dyeing Affinity of Regenerated Cellulose

At the outset the Committee hoped to be able to devise a simple technique for the measurement of dye affinity. Preliminary experiments were carried out with a few direct dyes on samples of viscose yarn taken from commercial production and also on specially prepared viscose yarn with a lower dye affinity produced by a steaming treatment. The dyeings were done at the boil in the apparatus described in the *Report of the Committee appointed by Council to discuss the Dyeing Properties of Direct Cotton Dyes*[1]. These preliminary experiments showed that, of the dyes examined, the most suitable was Sky Blue FF 200, but that the rate of boiling affected the degree and rate of dye absorption.

Further experiments were done using the above-mentioned apparatus, but under conditions of controlled boiling rate with specially prepared yarns spun with different degrees of stretch and from viscose of varying ripeness. The results obtained by the different committee members did not agree satisfactorily, and it was considered that the dyeing technique was mainly responsible. It was thought that mechanical agitation of the yarn during dyeing at a controlled temperature below the boil would give more consistent results.

One of the committee members already used a dyeing apparatus which was shown by the member to give reasonably consistent results, and which incorporated mechanical agitation of the yarn, accurate temperature control, and dye vessels fitted with reflux condensers. In view of this the Committee agreed to try out experiments on this type of apparatus. Differences in results were found this time to be connected with the type of photoelectric instrument used for measuring the dye exhaust liquors, and in particular with the filter used in the instrument. It was demonstrated by further experiments that the red impurity in Sky Blue FF 200 accentuated the difference due to the filters themselves. Three other direct blue dyes were examined with a view to finding a more suitable one in this respect than Sky Blue FF.

One dye, Durazol Blue G 200, showed to advantage in that with different photoelectric instruments, and different filters, dye affinity measurements were more reproducible. An assessment of the work to date indicated that different workers would not obtain dye affinity measurements with a reproducibility within $\pm 1{\cdot}5$ on an equilibrium value of approx. 50% unless precise dyeing conditions were used, together with a particular photoelectric instrument and filter. The precise dyeing conditions necessary involve the use of special dyeing apparatus with mechanical agitation of the yarn at a controlled rate, and temperature control with $\pm 0{\cdot}5$°C.

The Committee feels, therefore, that its work should now be terminated, since an absolute method of measuring dye affinity appears to involve such rigid control as to make it impracticable for routine use. Furthermore, the lack of a suitable cellulosic material of standard dye affinity precludes the use of a comparative method.

[1] J.S.D.C., **62**, 280 (1946); *Reports of the Committees on the Dyeing Properties of Direct Cotton, Vat, and Wool Dyes* (Bradford: the Society, 1952).

West Riding Section

Owing to the resignation of Dr. T. A. Forster from the Vice-chairmanship of the Section, Mr. R. K. Fourness has been invited to fill this office, and has accepted the invitation.

The Laska–Zitscher Laboratory

The rebuilt research laboratory of the Naphtol-Chemie Offenbach works of the Farbwerke Hoechst AG. was officially opened on 3rd September 1954. It has been named after the discoverers of the Naphtol AS dyes, the late Dr. L. Laska and Dr. A. Zitscher. On behalf of the President of the Federal German Republic, the Minister of Industry and Labour of the Land Hessen presented to Dr. Zitscher the Grosse Verdienstkreuz des Deutschen Verdienstordens. The President of the Gesellschaft Deutscher Chemiker, Professor Haberland, announced the forthcoming award to Dr. Zitscher of the A. von Baeyer Medal.

Mr. Fred Smith (*President of the Society of Dyers and Colourists*), announcing the decision to award the Perkin Medal to Dr. Zitscher, paid tribute to the work on azoic dyes. He mentioned particularly the scarlet–red–yellow range with excellent all-round fastness properties. Although these dyes were originally used for dyeing and printing cellulosic fibres, subsequently special methods had been worked out for their application to silk, cellulose acetate, polyamide and polyester fibres, and in certain cases wool and union fabrics.

On September 4th the works were open for inspection. Dr. Zitscher gave a lecture on the development of the Naphtol AS dyes and Dr. Kirst spoke on present-day methods for their application.

OBITUARY NOTICE

Robert Haller

Professor Robert Haller, one of the most eminent of Continental colourists, passed away at his home at Riehen near Basle on 21st July 1954, not long after his eightieth birthday. Haller entered on his career as a colourist immediately after graduating from the Swiss Federal Polytechnic at Zürich. He was chief colourist in the textile printworks of Gebrüder Enderlin at Traun in Austria from 1897 to 1915, and technical manager at the calico-printing works of Gebrüder Jentzsch at Grossenhain in Saxony from 1915 to 1928.

Empirical methods of working were still widely used in the industry at that period. Haller gradually replaced these with recipes and processes developed by research and experiment. Investigation of the scientific foundations of textile finishing became his life's work. A steady stream of papers from Haller's pen dealt with topical problems in textile chemistry, textile microscopy, and dye application, leading to his appointment as Professor of Textile Chemistry at the Technische Hochschule in Dresden, a position which he occupied from 1926 to 1928. Financial setbacks and illness in his family induced Haller to return to his native Switzerland. The Society for Chemical Industry in Basle (today Ciba) availed themselves of his services as head of their experimental textile printing and cellulose research laboratories. For a short period, Haller also taught at the Swiss Federal Polytechnic in Zürich. He went into retirement in 1941, but continued as an active research worker right down to the very last years. Among his best known publications are— *Handbuch des Zeugdrucks* (1927), *Chemische Technologie der Baumwolle* (1928), and *Färberei und Zeugdruck* (1951), as well as numerous papers on cotton, Indigo, Turkey Red, thickeners, etc.

Professor Haller has had an extraordinarily formative influence on the textile chemistry of the first half of this century. Throughout life he enjoyed general recognition as a leading authority, more particularly on textile printing. Indeed, those who from time to time have found themselves unable to accept his views will hardly deny this great leader in the field of textile colouring their unreserved admiration.

E. A. KRÄHENBÜHL

New Books and Publications

Technologie der Färberei und Textilveredlung

By Albert Schaeffer. Pp. xx + 808. Heidelberg: Melliand Textilberichte. 1954. Price, DM 73.80.

This book is a revised and extended edition of Volume I of *Handbuch der Färberei und anderer Prozesse der Textilveredlung*, reviewed in this *Journal* in 1949 (**65**, 538), and most of what was said in the original review is still applicable.

The author states that the book is intended to be a "source book for colourists, textile chemists, finishers, and salesmen, as well as a textbook for students", and certainly this large work is comprehensive, ranging over the origins of fibres, their preparation and textile processing to yarns and fabrics, bleaching and finishing, dye nomenclature and classification, processes of dyeing with different types of dyes, dyeing methods used for various textile materials, and finally dyeing machinery. Each section is followed by a generous bibliography, which sometimes exceeds in length the preceding text, but since there are no cross-references between the text and the bibliography, the reader is left to find the authority for any particular statement for himself. The author tells us that there are over 4300 references in all, and these occupy about 100 pages of the book. Three indexes take up a further 100 pages (including advertisements), while there are extensive tables of brand names and a general classification of dyes and auxiliary products occupying roughly a further 150 pages. In addition the book is well illustrated with photographs and diagrams of machines.

With regard to the text, this is in most cases a straightforward account of the processes concerned. Modern dyeing processes are described, but there is no attempt to discuss any aspect in a critical or constructive manner, so that the reader is left completely in the dark as to the relative merits, for instance, of the pad-steam process, the Williams hot-oil process, photochemical development of leuco vat esters, and the Standfast molten-metal process for the application of vat dyes. Similarly, in the section on the dyeing of polyester fibres, the reader is informed in separate short paragraphs that the fibres may be dyed with disperse, azo, vat acid, or vat leuco ester dyes, but no indication whatever is given that some of these processes may be difficult or even impracticable. Such information is worse than useless to the serious student, and only the elementary student is likely to benefit from the excellent and comprehensive general review of textile processing and dyeing. Numerous misprints in product names and errors in their description detract from the value of the book as an encyclopædia of dyeing.

T. VICKERSTAFF

Reports on the Progress of Applied Chemistry Volume XXXVIII 1953

London: Society of Chemical Industry. [1954.] Pp. 989. Price, 40s. 0d. (20s. 0d. to S.C.I. members).

The volume for 1953 follows the usual pattern, reviewing the progress made in— fuel and fuel products; organic and inorganic chemistry; biological products; textiles, plastics, adhesives, and

paints; food, agriculture, and horticulture, including starch and brewing processes; and chemical engineering and water treatment. It contains 7416 references, many of them composite. In the chapter on *Intermediates and Dyestuffs* R. K. Fourness and E. Stead state that the total number of patent specifications claiming improvements in the manufacture and application of dyes and intermediates published in 1953 was only slightly less than in 1952, with a decrease in the number of specifications relating to anthraquinonoid vat and disperse dyes and an increase in those dealing with phthalocyanine derivatives. They give as the two important developments—(1) the premetallised dyes for wool and nylon carrying sulphamyl instead of sulphonic acid groups and (2) a water-soluble colourless compound which is condensed on the fibre in the presence of a metal salt to produce a phthalocyanine. As shown in Table I (p. 97) exports of dyes have risen in 1953, with Germany again leading in quantities but with Switzerland exporting the greatest value of dyes.

In his review on *Cosmetics and Toilet Preparations* F. Atkins points out (p. 163) that, whilst in the years following the war many of the raw materials for the cosmetic industry were subject to import-licence restrictions, during the last two or three years the position has much improved, and some of the raw materials, like triethanolamine, propylene glycol, and its fatty acid esters, are now more readily available and many are manufactured in the United Kingdom. He also refers to the controversy on chlorophyll and quotes the article by W. Mitchell (*Mfg. Chem.*, **24**, 139 (1953)), which can be briefly summarised—natural chlorophyll has no deodorising powers, but water-soluble derivatives, the so-called chlorophyllins, have, and the whole argument concerns the chlorophyllins and not chlorophyll itself.

K. Burrow reports on *Detergents* (p. 365)—the raw materials, manufacturing processes, and additives; he mentions the increased use of methyl cellulose as additive to synthetic detergents, as it tends to counter the harsh action of some of the synthetic detergents on the skin (Stephens, *Chem. Prod.*, **16**, 299 (1953)). A number of papers have recently been published on the evaluation of detergents (Harris, Vaughn, Compton and Hart), but in many cases such tests are empirical and only a few are a substitute for practical tests that imitate the conditions obtaining in actual use.

The chapter by A. E. Stubbs on *Cellulose Textile Chemistry* is devoted to a review of the bleaching, dyeing, and printing of cellulosic materials, and, as no comprehensive review on these subjects has been published in these *Reports* since 1950 (covering 1949), and the scientific and technical literature on these subjects is now so large, he confines his review (pp. 458–476, with 174 references) to the more salient features of the developments that have taken place since 1949 and refers for more detailed coverage of the literature to *Review of Textile Progress* (published jointly by the Textile Institute and our Society). He mentions that continuous bleaching methods based on sodium chlorite are not now used so much for cotton bleaching as on special-mixture fabrics (e.g. those containing cellulose acetate or nylon), rayon staple, and linen. He describes the recent developments in package dyeing (e.g. high-temperature dyeing machines) and in continuous dyeing methods for piece goods, with the Standfast molten-metal process and its assured success and advantage for the vat dyeing of cotton and rayon piece goods. Up to the time of writing the report, twelve such machines had been installed. The American hot-oil process for the fixation of vat, sulphur, and direct dyes and the Williams-unit dyeing method are also discussed, and so are the contributions by Vickerstaff, Marshall, Peters, Michie, and Thornton on the equilibrium adsorption of vat dyes on cotton and the rates of reduction and redox potentials of vat dyes.

In his review on *Non-cellulose Textile Chemistry* (pp. 477–496, with 303 references) F. O. Howitt mentions no outstanding development but reports steady progress in research on wool, its structure, chemical properties, shrinking and felting, scouring, bleaching, dyeing, and finishing. He also refers to the recent literature on regenerated protein fibres, nylon, and Terylene, and to the increasing importance of fibre blends.

In the chapter *Sewage, River Pollution, and Trade Wastes* E. L. Streatfield reports (p. 825) that the effect of synthetic detergents on sewage treatment continues to receive considerable attention, as they have a tendency to reduce the efficiency of flocculation and sedimentation and by lowering surface tension to cause foaming in aeration tanks. He refers particularly to the contribution on this subject by P. C. G. Isaac (*Wat. Sanit. Engr.*, **3**, 413, 453 (1953)).

The author and subject indexes are of the usual high standard. The volume is again well printed and produced, and is a fount of stimulating knowledge.

A. F. KERTESS

The Chemistry of Synthetic Dyes

Volume II

By K. Venkataraman. Pp. xv + 705–1442. New York: Academic Press Inc. 1952. Price, 120s. 0d.

The completion by Professor Venkataraman of the second of the two volumes of his treatise provides a comprehensive and critical survey of dye technology for use by both the academic and the industrial worker in this field. Although there is special emphasis on the structure, preparation, and properties of dyes, all interested in synthetic organic chemistry will find in the two volumes much to consult and study.

Whereas Volume I, published early in 1952, covers mainly intermediates, azo dyes, colour measurement, and the effect of chemical constitution on colour, Volume II deals with anthraquinone dyes, phthalocyanines, cyanine, azine, sulphur, indigoid, basic, and other miscellaneous groups of dyes. It covers the action of light on dyes and dyed fibres, chemical constitution of dyes in relation to substantivity, and identification, analysis, and evaluation of dyestuffs.

This second volume more than bears out the reviewer's earlier opinion (J.S.D.C., **68**, 354 (1952)) that Professor Venkataraman has achieved a classic work, and in this case there is even less to criticise than in Volume I. The subject matter is in the main well proportioned, but there is a tendency in several chapters, perhaps naturally, for overemphasis in detail in fields in which the author has carried out research.

The largest portion of Volume II, about one-third, covers in very able fashion the field of anthraquinone chemistry, dealing in a series of seven chapters with anthraquinone dyes for cellulose acetate, mordant dyes, anthraquinone acid dyes, solubilised vat dyes, and the classification, standardisation, properties, and application of anthraquinone vat dyes. The up-to-date treatment of the vast field of anthraquinone dyes is no mere catalogue of constitutions. Here, as in other portions of the book, German information reported in *B.I.O.S.* and *F.I.A.T.* publications has been adequately blended with material chosen with laudable discrimination from the patent literature to make for the expert what is, without doubt, an important reference volume. In these chapters details of constitution, synthesis, manufacture, and application of groups of dyes are so interwoven as to make even for those unacquainted with this essential branch of dye technology an immensely interesting and absorbing study.

The chapter on the di- and tri-phenylmethane dyes gives too little information on the important group of Fanal (phosphomolybdotungstic) lakes used extensively in printing inks, and no distinction is given between the various brands manufactured. The chapter on azine dyes provides an adequate description of the direct cotton dyes of the dioxazine series, in which there has been great activity.

Starting with the early Ionamines for dyeing cellulose acetate, there is then listed a complete colour range of substituted aminoanthraquinone derivatives (Cellitons, Duranols) with properties and methods of preparation of numerous examples. This is followed by a description of the development of the water-soluble Solacet dyes (the sulphuric esters) and also other methods of solubilisation. Finally, there is a well referenced section on gas-fume fading. Alizarin, its lakes, other hydroxyanthraquinones, and the natural anthraquinone colouring matters are dealt with in a short chapter.

Indigoid and thioindigoid dyes are treated fully in a lengthy chapter with a useful introductory classification of the various types manufactured. The chemistry and the synthesis of indigo are well described, including the manufacturing process for phenylglycine.

Recent developments, methods of preparation, and details of application of the solubilised vat dyes— the Soledons and Indigosols (Anthrasols)— are described and tabulated to show their identity with each other and their relationship to the parent vat dye.

Details of processes for the various types of sulphur dyes are given in another chapter, followed by classification of numerous commercial brands grouped according to colour. The whole forms a comprehensive review of the preparation, properties, and application of the available extensive range of these low-cost dyes for cotton. In addition there is a detailed account of the mechanism of formation of sulphur dyes and a review of numerous attempts to elucidate their constitution.

The various groups of cyanine dyes, which are of great interest as photographic sensitisers, are dealt with, and full-page charts detailing methods of preparation of several of the more important dyes are given in a chapter devoted to this subject.

Miscellaneous dyes, including dyes derived from naphthalic acid, colour formers for photography, fluorescent and luminescent dyes, and lacquer colours, are grouped in a separate chapter.

Apart from the structure, preparation, and properties of the pigmentary forms of the phthalocyanines (Monastrals), dye chemists will be interested in the sections on the phthalocyanine derivatives, mainly in solubilised form, in which technical development has been extensive during the last few years. New products described include sulphonated copper phthalocyanine for direct cotton dyeing of excellent fastness properties, dyes for lake making, spirit-soluble lacquer dyes, and sulphur dyes of outstanding light and chemical fastness, and mention is also made of attempts to make vat dyes. Chloromethylated copper phthalocyanine converted into a temporarily soluble form gives a beautiful turquoise (Alcian Blue 8G, ICI) for calico printing. During steaming the solubilising component is decomposed, and the insoluble pigment fixed on the fibre.

Chapter XL, which is concerned with the action of light on dyes and dyed fibres, is of mixed value. One would expect to see much more written on the interesting and technically important aspect of the relationship between chemical constitution of dyes and their fastness to light. The very short sections on some of the classes of dyes are of limited value. Conciseness leads to semi-valid generalisations, from which inaccuracy can often arise. The section on pigments is not very helpful. There is barely a sentence in this portion which will stand up to critical examination. In reality, the paucity of data or the correlation thereof emphasises the present dearth of precise knowledge of fastness to light and its relation to chemical constitution. The greater portion of this chapter consists of a profusely tabulated and well documented account of the degradation of cellulose dyed with yellow and orange vat dyes, with factors affecting light tendering, the mechanism of the activity of vat dyes in tendering, and the relationship between chemical constitution of these dyes and their tendering activity. The reviewer would like to see the section on light fastness rewritten to the same excellent standard.

In the next chapter there is a lengthy and very interesting review of the chemical constitution of

dyes in relation to substantivity, mainly on cellulose, prefaced by a section on the constitution of cellulose and on the structure of cellulose fibre. It ends with a section on the affinity of dyes for wool. Theoretical considerations are discussed in the case of all the main groups of dyes, and the various theories relating to the configuration of dyes and their substantivity are critically examined. From all angles this is a very good chapter.

The identification, analysis, and evaluation of a dye are of importance, and the author has taken great pains to make the chapter of nearly 50 pages dealing with these topics of marked practical value. The various chemical classes of dyes are tabulated, and the Green–Clayton scheme for their identification is discussed fully. Quantitative analysis by chemical, colorimetric, and dyeing methods is given some mention. It is not an easy task to make the subject of analysis one of absorbing interest, but this chapter is made eminently readable by the fairly lengthy, well referenced, and diversely exemplified section on chromatography. This forms an excellent review of the application of chromatographic analysis to coal-tar hydrocarbons, intermediates, and dyes. It discusses with extensive extracts from researches the correlation of chemical constitution and chromatographic behaviour, and deals with the adsorbability not only of dyes, but *inter alia* of isomeric nitro compounds, aminoanthraquinones, and various *cis–trans* isomers.

The volume concludes with some 90 pages covering author, subject, and dye indexes for both Volumes I and II.

In this volume, as in Volume I, there is a combination of the theoretical side discreetly merged with the technical aspect to give a realistic and up-to-date picture of present-day dye manufacture and dye technology in all groups of dyes. Its practical outlook has already made this treatise singularly attractive to those engaged in the vast field of dye chemistry. As a standard book on the subject it may not be omitted from the shelves of university and industrial libraries.

J. GLASSMAN

Condensed Pyridazine and Pyrazine Rings
(Cinnolines, Phthalazines, and Quinoxalines)

By J. C. E. Simpson. Pp. xvi + 394. New York and London: Interscience Publishers. 1953. Price, 100s. 0d.

This is the fifth volume, with Arnold Weissberger as Consulting Editor, in a series of monographs devoted to the chemistry of heterocyclic compounds. Its British author, the late Dr. Simpson, was a recognised world authority on the cinnolines; he completed the manuscript for this monograph, but did not live to see its publication.

The book reflects great care and thoroughness in the compilation and presentation of data related to the compounds reviewed. It is carefully produced with a most generous provision of formulae, which serve to make the text readily understandable. Some lack of consistency is shown in the representation of the aromatic nucleus, often on the same page, but without ambiguity. The compounds are conveniently assembled in some forty tables giving their physical properties and related derivatives, together with full literature references. The arrangement of the references at the end of each chapter shows the scope of the work but leads to much duplication, often on facing pages. For the period before 1917, but only in the case of quinoxaline, the references must be supplemented by Meyer–Jacobson's *Lehrbuch der organischen Chemie*, Volume **2**, Part III. Otherwise, complete references are given for the period up to the end of 1948, although in some cases more recent work is included.

The book shows little outside an academic interest in the compounds, although much of Simpson's own development of the cinnolines was based on the search for potential antimalarials. Some quinoxaline cyanine dyes are reported, and mention is made of an early observation on the antibacterial action of cinnoline against *Escherichia coli*. There is some discussion of the chemiluminescence of phthalazine derivatives, e.g. luminol (5-amino-1:4-dihydroxyphthalazine).

Trivial reference is made to the azaquinoxalines in two pages, but this important field, so recently developed, is to be fully discussed in a later monograph. Some criticism must be made of the variety of methods employed to formulate quaternary salts, especially of the numerous examples where the representation could be interpreted as a quinquevalent nitrogen.

This book is especially valuable for its academic review of important ring systems, and for such a purpose has proved to be complete and accurate.

G. R. RAMAGE

Compounds with Condensed Thiophen Rings

By H. B. Hartough and S. L. Meisel. Pp. xv + 515. New York and London: Interscience Publishers. 1954. Price, $16.50.

Dr. Weissberger's series of monographs on the chemistry of heterocyclic compounds now needs no introduction, volumes having appeared with consistent regularity over the last few years, and this seventh volume maintains the high professional standards set up by its predecessors. Chapter I discusses in some detail from a theoretical standpoint the factors influencing the chemical reactivity and substitution of the thiophen systems and emphasises the predominant effect of the sulphur atom, while at the same time comparing them with the corresponding furan and selenophen systems. Chapter II, the longest in the book, deals with the voluminous literature on thionaphthen and its derivatives, including many of the basic intermediates used in the manufacture of thioindigoid dyes. In spite of all the large amount of work recorded, it is surprising how ignorant we still are of much of the elementary chemistry of these compounds. The chemistry in this field, especially on the synthetic side, is truly fascinating, and it is remarkable that our academic chemists have so long left its study almost entirely to the industrial chemists.

The chapter of most immediate interest to readers of this *Journal* is that dealing with thioindigo and related dyes. As the authors point out, on account of the very extensive technical and patent literature, of which there is a good bibliography, this section is not intended to be exhaustive. The chemistry of these dyes is very adequately discussed, but such information as is given on commercial dyes (limited almost entirely to a single table), although in the main correct, is very limited and out of date, and is obviously taken from an ancient compilation. There are interesting subsections on the factors affecting the colour of thioindigoid dyes and on indophenin and related dyes. The bibliography on the sections on dyes appears to be reasonably complete, but it is surprising that no reference is made to published textbooks and monographs, e.g. Martinet's *Les Indigoïdes*, dealing specifically with that part of the subject not completely covered by the present monograph.

Subsequent chapters, comprising about half the book, deal with dibenzothiophen and its numerous derivatives, naphthothiophens including thiophenanthraquinone and its derivatives, and the various systems containing three or more carbocyclic or heterocyclic fused rings. Finally there is a short chapter on condensed selenophen and tellurophen systems.

Authors and publishers alike are to be congratulated on this worthy addition to post-war chemical literature, but what a pity that its price puts it quite out of reach of individual chemists!

S. Coffey

Pigments

Their Manufacture, Properties and Use

By J. S. Remington and W. Francis. 3rd edition 1954. Pp. xv + 222. London: Leonard Hill Ltd. Price, 20s. 0d.

There are so few modern books on pigments that all connected with the pigment industry look forward with interest to the publication of a new book, or the revision of an existing text. Hopes that J. S. Remington's book would be substantially improved by revision in collaboration with W. Francis have been disappointed.

Treatment throughout is very uneven. Thus, inorganic pigments receive 170 pages and organic colouring matters 25 pages of which 4 are devoted to inorganic bases. Within each main division there is similar unevenness both in quality and in quantity. White lead receives detailed treatment, whilst the much more important titanium dioxide receives less than a third of the space and contains no clear reference to the improved properties associated with the preparation of this pigment in the rutile crystalline form. Possibly the sentence on page 53 containing the phrase " . . . titanium dioxide made from rulite . . ." [*sic*] is intended to cover this important development. Similarly, one looks in vain through the 10% of the book devoted to Ultramarine for reference to modern work on improving acid resistance.

Irrelevant and loose statements abound and it would be tedious to catalogue them. Much space is occupied by formulae for pigment manufacture of negligible value. The chapter on Organic Colouring Matters contains many inaccurate statements.

All in all, this is not a book to be recommended except as an elementary survey of the pigment field for those not likely to be directly concerned with it.

D. M. Stead

Du Pont

One Hundred and Forty Years

By William S. Dutton. 3rd edition 1951. Pp. x + 408. New York: Charles Scribner's Sons. Price, $5.00.

The first edition of this book was published in 1942 to record, as its title indicates, the growth and myriad expansion of the du Pont business from the gunpowder factory which Eleuthère Irénée du Pont de Nemours established near Wilmington, Delaware, in 1802. With the addition of an Epilogue covering the activities of the company in World War II and onwards, the third edition appears appropriately to mark the sesquicentenary of a company unique in American industry. It is a competent, colourful, and well written story, ranging from Irénée du Pont's contacts with Lavoisier to the development of nylon, and its impressive picture of the achievements of the du Pont family and of the wisdom and judgment, as well as vision, which successive generations of that family have consistently displayed in their business activities should correct some false connotations of the name du Pont. To the members of this Society the fourth book, in which Mr. Dutton outlines the way in which du Ponts' entered on the manufacture of dyes and intermediates and thus into organic chemicals, including rubber chemicals, pharmaceuticals, detergents, etc., and then into the fields of pyroxylin lacquers, synthetic resins, rayon, synthetic rubber, and nylon, will be of special interest. The account is readable and balanced. Mr. Dutton has an eye for the picturesque or dramatic but never strays into sensationalism, nor is the detail allowed to obtrude to the point at which it becomes tedious.

The book is claimed to be a biography of a business and of a young nation on the march. The second claim may be challenged. Even in the most vivid earlier chapters sufficient background is scarcely given for that to be conceded, as will be apparent to anyone familiar with Donald McKie's recent biography of Lavoisier. With regard to the first, it might perhaps be better to speak of it as a business autobiography, if such a term be permissible. Mr. Dutton himself claims that it is a record of the du Pont company as seen by du Pont men—in other words, an inside view. It is a picture of a company as seen by living members of that company, themselves carrying on its activities, its traditions, its philosophy. As such it has the advantages and also the drawbacks of autobiography. It can be described as history only

in the sense in which R. G. Collingwood regards history as concerned not with mere phenomena but with things which the historian looks not at but through to discover the thought within. This book gives us a clear record not merely of the activities of the du Pont company during a century and a half, but also of the ideas and the philosophy or principles which guided those activities and that expansion. The task, as already stated, has been done competently. The pity is that it could have been so much more. The complete absence of any reference to internal or external sources of information robs it of any serious claim to scholarship. As a source book it will be of little value to the industrial historian; as publicity, at least in the better sense of propaganda, it may well be excellent; as a contribution in the sphere of public relations its value is more doubtful; as a contribution to industrial history, like so many other house portraits written to celebrate similar occasions, it falls sadly short of the mark.

R. BRIGHTMAN

New Fibres from Proteins

By R. L. Wormell. Pp. xx + 208. London: Butterworths Scientific Publications. 1954. Price, 32s. 6d.

The publication of Dr. Wormell's book marks a milestone in the literature on the chemistry of high polymers. It is basically a historical survey of the development of regenerated protein fibres, and shows how the subject has been raised from the empiricism of Ferretti to the logical approach to protein and polypeptide regeneration during the last few years. Throughout this period of time, Dr. Wormell has played a vital rôle in the development work.

If the philosophical aspect of the publication is part of the author's conditions for writing this book, then we must accept it, as we are thus allowed to delve into the more practical aspects of a very interesting subject. I personally would prefer the book shorn of its metaphysics, and the space thus saved used for an amplification of the experimental data. In particular, the subject matter on p. 65 should have been expanded and the equations given for the calculations of yarn denier in spinning. Outside the expert field the basic principles of the extrusion of filaments appear to be little understood.

I cannot agree with all the author's theoretical deductions but, as Dr. Wormell himself points out many of the shortcomings of his own and other theories of protein structure, I will leave this with no further comment. It is, however, in the treatment of his experimental data that Dr. Wormell gives the reader an insight into the comprehensive research project that he has carried out over the last twenty years: we have in effect a summary of what might have been many important papers on the structure and the regeneration of proteins. On account of industrial necessity, these papers have been replaced by many patent specifications; it appears a great pity that references to the patents have been numbered only and the actual names of the patentees omitted. The author's contributions would then have been clearly obvious.

I have read the book with great interest, and have reviewed it in the light of my previous knowledge of the subject and the author. Although in my opinion it does scant justice to the work and the discoveries of its author, it nevertheless should be read by all students of protein structure with the realisation that here is a very abridged account of the main life's work of an industrial research chemist.

F. HAPPEY

The British Rayon and Synthetic Fibres Manual

Published in association with the *British Rayon and Silk Journal*. 2nd edition 1954. Pp. ix + 364. Manchester: Harlequin Press. Price, 30s. 0d.

Although many hands make light work, there is the risk of too many cooks spoiling the broth. A quantum of ten scientists and technologists have collaborated to make the present book, which shows many of the good and few of the bad features of collaboration.

With two exceptions only, each author is responsible for a separate chapter. As a consequence there is much variety of style and treatment. Some of the chapters are broad, sweeping reviews, whilst others go elaborately into details of adjustments of machines. In a similar way some of the diagrams are designed for novices and others for students. In the chapters on fibre manufacture, dyeing, and chemical considerations generally the treatment is in the form of broad surveys. In the chapters on weaving and mechanical processes the treatment is detailed. It follows that the book is particularly suited to a spinner or weaver who wishes to read of his own work in the context of the previous and subsequent processes. This is not to say that the book is unsuitable for more general reading: it is suitable.

Compared with the 1947 edition, this second edition sells at a 43% higher price and contains 47% more pages. It runs through the whole gamut of processes with special emphasis on man-made fibres. Current topics are considered and generally it appears to be up to date, but it is difficult to be more positive concerning this book, as it covers such a wide field. There is a minor exception in the reference to cuprammonium yarn on p. 128, which may mislead someone who does not know that its manufacture in Britain has been discontinued. Not many mistakes have been noticed, but there are a few misleading phrases. For example, the statement on crystallinity on p. 19 disagrees with much published work, and on the same page the impression is given that Fortisan is a cellulose acetate yarn. Again there seems to be no justification for the remarkable generalisations about the affinity and the refractive indices of viscose rayon yarn on p. 62.

The book has been written and revised by a panel of experts, and it would be surprising if anyone could read it without learning something of interest. It can be recommended.

J. M. PRESTON

Nylon Technology

By Karl H. Inderfurth. Pp. ix + 335. London: McGraw-Hill Publishing Co. Ltd. 1953. Price, 46s. 6d. ($7.00).

This is the third volume in a series of books on textile technology; the two previous ones have dealt with Rayon Technology (including acetate rayon) and Fabric Defects.

Like so many modern books the present one has been written by a number of authors, including six specialists in their own fields. Technical service information obtained from the du Pont company has been freely drawn on as well as that from hosiery, stocking, and outerwear manufacturers. The author in the preface writes that it should be immediately obvious that a book encompassing such a wide scope could not be adequately covered by one individual.

The book consists of fifteen chapters and an introduction; the latter gives a review of the American development of nylon from 1935 to 1950, from the test-tube development to the latest plant at Chattanooga.

The first chapter deals with the chemical and physical properties of nylon and the action of heat, humidity, and similar agencies; it discusses also the shrinkage of nylon during processing.

Chapter 2 deals with the spinning of nylon on the cotton system, while Chapters 3 and 4 are devoted to the spinning of nylon staple on the worsted and woollen systems. In these three chapters the effect of product variations such as crimp, staple length, and finish are dealt with, while the spinning proper covers the operations of blending, tinting, packing, carding, drawing, and spinning even to the spooling and coning.

Chapter 5 deals with the preparation by the throwster of yarn suitable for weaving and tricot manufacture, including the operations of preshrinking, winding, throwing, and single-end-sizing, together with the ancillary operations of size preparation and tinting. This chapter lists the common faults found in cones and the method of obviating them.

Chapter 6 is devoted to the preparation of continuous-filament as well as staple-fibre nylon warps on the high-speed cotton system and the worsted system. Polyacrylic and polyvinyl acetate sizes are described, together with the use of slasher yarns which have been single-end-sized and oiled before warping. The chapter lists the properties of a good size and also details the method and optimum temperature for slasher sizing on the seven-can system.

Chapter 7 deals first with the complementary operation of pirning of weft and with the weaving of nylon. Methods for overcoming pirn taper barré are outlined.

Chapter 8 is devoted to full-fashioned hosiery knitting. It includes the latest American knitting practice and test methods for checking the product. Looping, seaming, inspection, preboarding, scouring, and dyeing are dealt with and recipes given for scouring baths and for dyeing light and heavy shades. The chapter also includes information on stripping and bleaching where necessary, and finishes with the final boarding operation. Details are also given of the Dunn system. Twenty of the chief defects usually found in stockings are outlined, the reasons for them given, and photographs shown to illustrate the defect.

Chapter 9 outlines the knitting of staple yarns on half-hose machines, outerwear knitting, heat-setting of the finished garments, and piece dyeing.

Chapter 10 deals with tricot knitting on high-speed machines and gives the best yarn tension devices, machine settings, and the principal causes of defects in the grey.

Chapter 11 is devoted wholly to the manufacture of tyre cord.

Sewing thread is dealt with in Chapter 12, which compares the methods of manufacture by the orthodox process and that of the Belding Corticelli Corporation.

Chapter 13 deals with the scouring of nylon fabric prior to dyeing and with the dyeing of nylon with a number of common disperse, acid, and chrome dyes.

The printing of nylon occupies Chapter 14 and a number of typical printing paste formulae are given.

Finally, Chapter 15 is concerned with the finishing of nylon fabrics, the removal of tint and size, and the elimination of wrinkles prior to finishing. Heat setting by the hot-air method and the heated-roll machine is detailed. The radiant-heat method of setting is also described, and temperatures and times are given. Bleaching and tinting of grey fabrics following possible overheating are described, together with the application of finishing agents such as semi-lubricants, antistatic agents, and resins.

The book has been compiled by men familiar with the "know-how" of nylon processing and is to date one of the most valuable contributions to the literature of nylon technology. It is a useful reference book for all those who are interested in the handling of nylon yarns and fabrics. The data would appear to be correct, and while the book covers only 300 pages, it contains material of interest to technologists in a number of fields. It gives all the essential details required by the mill man and is written in a style easy to read and understand.

G. Loasby

Fuel Conservation

Productivity Report on the Conservation of Fuel, Heat, and Power

London: British Productivity Council. 1953. Pp. xii + 102. Price, 5s. 0d.

The report bearing this heading is that of a British specialist team which visited the U.S.A. in 1952 under the auspices of the Anglo-American Council on Productivity for the purpose of studying the application and conservation of fuel, heat, and energy with a view to improving the efficiency of fuel utilisation in Great Britain and indicating ways and means by which a national fuel policy might be developed.

The report briefly reviews the acute fuel position which has obtained in this country for many years past and particularly the disaster of 1947, our coal

reserves, and the work of the Ministry of Fuel and Power in the fuel economy field.

The fuel resources of the United Kingdom and the U.S.A. are compared, and attention is directed to the very favourable fuel position in the U.S.A., where not only are the reserves of immense proportions but where also 50% of the coal output is obtained from thick seams near the surface and is therefore easily mined. In addition, the exceptional resources of oil, natural gas, and water power are commented upon, and their important contribution to U.S.A. economy is emphasised. The great advantage of the U.S.A. as regards fuel resources is emphasised when one compares those of the United Kingdom, where coal is still the major source and even that appears to be of decreasing intrinsic value, as well as being more difficult to mine because of the depth of the workings and much lower thickness of the seams.

The distribution of fuel supplies is commented upon, and one is impressed by the great development of pipeline distribution services for liquid and natural gas fuels. Distribution by this means is very convenient and has developed to such a stage that pipelines are now in fact considered a major form of transport.

An important chapter deals with the wastage of steam and power in three industries particularly, viz. brewing, textile, and paper, and gives references to the economies to be effected by, for instance, reduction of process steam pressure, generation of back pressure power, thermal storage, elimination of peak loads, heat insulation, etc. Many reports of other teams who have visited the U.S.A. have commented upon the more extended use of mechanical handling and the use of power generally in order to ease the demand for human effort, and this report fully confirms those previous observations and the savings which are consequently made by this more extensive use of power.

The report directly draws attention to the average efficiency in generating stations, where some 70% of the heat in the coal burnt is wasted in cooling towers or dissipated by other means. The advantage of dual-purpose generating stations, i.e. those which supply both heat and power, and the consequent increase of efficiency to 70% instead of the present 30%, are noted. Examples of dual-purpose stations, both existing and contemplated, are briefly described, and the operation of one or two of these stations in the U.S.A. is dealt with in some detail.

In the succeeding chapters fuel conservation as applied to some of our industries is reviewed, and methods by which the fuel might be saved are dealt with.

In the more general field of fuel conservation it is pointed out that the Lancashire type of boiler is practically unknown in the U.S.A., where water-tube boilers are the rule rather than the exception even in the smaller industrial installations.

The importance of treatment of boiler water, instrumentation, staffing, etc. is briefly dealt with, whilst the loss through uncontrolled space heating and from uninsulated buildings is emphasised.

Finally, the report deals with the very vexed question of smoke emission and gives some details of the stringent regulations which obtain in the U.S.A., not only as regards the emission of smoke but also as regards the type and design of fuel-consuming plant which is installed. Unlike most reports, the summary and the recommendations are at the beginning, and correctly draw attention to the fact that there is no room for complacency on the question of fuel conservation, and that thirty million tons of coal per annum could be saved by reformed practices and better utilisation. The recommendations— of which there are forty— form the key to this most important of present-day problems— fuel conservation.

W. A. WORDLEY

Manufacturers' Publications and Pattern Cards

The Society does not accept any responsibility with regard to the statements in the following notes. Any publication abstracted may be referred to by members of the Society on application to Dr. C. B. Stevens, Dyeing Department, Leeds University

Ciba Ltd.

CIBALAN BLUE 3GL— This further addition to the range of the 2 : 1 dye : metal complex type of premetallised dyes is described in a supplement to Pattern Card No. 2570. It has similar dyeing characteristics and is recommended for the same purpose as the other members of this class of dye. Fastness figures include— Light 6–7, carbonising 5, alkaline milling 4.

The Geigy Co. Ltd.

IRGALAN RUBINE RL: IRGALAN VIOLET 2BL— Two additions to the Irgalan range of 2 : 1 dye : metal complex type of premetallised dyes are described in this card. Both are recommended for use alone and in mixtures with other members of the Irgalan and Irganol S ranges on wool, silk, and polyamide fibres. A feature in each case is the relative brightness of hue, Rubine RL giving bright bluish reds and Violet 4BL reddish violets. Fastness figures on wool include— *Rubine RL:* Light 7, heavy milling 5, perspiration 5. *Violet 4BL:* Light 6–7, heavy milling 5, perspiration 5.

Imperial Chemical Industries Ltd.

TECHNICAL INFORMATION LEAFLETS— *Dyehouse No. 206. Textiles for Insulating and Covering Conductors of Electrical Cables and Wires (Post Office Specification M109D).*

Dyehouse No. 195— Woolen and Worsted Color Card of America: Fall and Winter 1954.

Dyehouse No. 208— Colours for Phenol–Formaldehyde Moulding Powders— A range of dyes is given, selected as having the best technical performance and giving pleasing colours under laboratory conditions of test. Figures for fastness to light, heat, water and soap, and ethanol and amyl acetate are appended.

Dyehouse No. 210— Lead Chromes in Paint.

Dyehouse No. 212— The Effect of Rubberproofing on Dyed Acetate Rayon, Nylon, and Terylene Polyester Fibre Fabrics— Details are given of the behaviour of the Duranol, Dispersol, and Multamine dyes recommended for dyeing acetate rayon, nylon, and Terylene when the dyed material is subsequently rubberised using the "cold

cure", "hot air cure", and "open steam cure" processes. It is noted that inclusion of either Tumescal D or Tumescal OP in the dyebath has no significant influence on the effect on the colour of either the cold cure or the hot air cure, but the effect of the open steam cure may be a little more severe. The dyes present do not materially affect the rate of degradation of the rubber.

Dyehouse No. 213— The Waxoline Red OS Test— A Works Control Method for Wool Scouring Processes— The test consists essentially in treating a sample of the wet scoured material in a dilute aqueous dispersion of Waxoline Red OS and assessing the colour developed by absorption of the dye by the residual oil.

Dyehouse No. 214 (replaces No. 157)—*Croceine Scarlet printed on Nylon*— The yellow stains which tend to arise during steaming are due to the presence of a yellow by-product the production of which is promoted by the use of Crystal Gum. Addition of ammonium oxalate and sodium chlorate to the printing paste previously recommended prevents staining.

Dyehouse No. 216— Caledon Printing Yellow 6GS Paste; Avoidance of Prints showing Excessive Greenness— A combination of low alkali and high Formosul content in the print paste promotes greenness, particularly when the dye content also is high. The potassium carbonate content should not be less than 100 g./kg. and the Formosul content should not exceed 150 g./kg. A mixture of hydrogen peroxide and ammonia is recommended for oxidation.

Dyehouse No. 217— The Prevention of Over-reduction of Vat Blues in the Pad–Steam Vat Printing Process— Addition to the printing paste of either thin-boiling white maize dextrin, sodium nitrate, or sodium chlorate has been found to eliminate completely the risk of over-reduction.

Dyehouse No. 219— Fastness to Anti-crease Processing of Acid Dyes printed on Spun Viscose Rayon by the Urea Process— Thirty-four acid dyes recommended for printing viscose rayon by the urea process have been examined for their suitability for anti-crease processing. The test method employed is detailed, and the figures obtained are tabulated together with figures for the fastness to light of the dyed material with and without a crease-resist finish.

Dyehouse No. 220— Removal of Linseed Oil Sizes— Treatment at 120°F. followed by further treatment at 212°F. in a solution containing Lissapol N, Lissapol C Paste, sodium carbonate, and either sodium perborate or percarbonate is recommended.

Dyehouse No. 221— Knitting Oils— This leaflet describes a self-emulsifiable, self-scouring lubricating oil, based on Lissapol NX and Lubrol MOA, for applying to the needles of knitting machinery.

Dyehouse No. 223—Coloured Laundry and Textile-marking Inks— Inks having an adequate degree of permanence on cellulosic fibres may be prepared by simple mixing of selected pigment pastes, Bedacryl L, and water. Such inks are reasonably fast on wool, silk, nylon, and Terylene.

Dyehouse No. 224— Black Surface-dyed Nylon Monofilaments— Blacks of very good fastness to paint solvents and distemper media and to heat and light may be obtained with Solochrome Black WDFA applied by an after-chroming technique.

Dyehouse No. 225— Washing Formulae for the Bendix and Thor Washing Machines using Lissapol N–Cellofas B— Corrosion of aluminium and aluminium alloy components may occur if soda ash or common salt is present in the wash liquor. It is recommended that the latter be omitted and the former replaced completely, if possible, by sodium metasilicate.

Dyehouse No. 226— Anti-static Lubricants in Worsted Spinning— The use of Lissapol N for this purpose is described.

Dyehouse No. 227— 1955 Spring and Summer Color Card of America for Man-made Fibres and Silk.

Dyehouse No. 229— Woolen and Worsted Color Card of America Spring and Summer 1955.

Dyehouse No. 230— Oxidising Agents for Vat Dyes— A comprehensive series of tests is described using sodium percarbonate, hydrogen peroxide, ammonium persulphate, sodium perborate, and potassium dichromate under acid and alkaline conditions, and practical recommendations are made, based on the results obtained. Details are also appended of a gas-volumetric method of estimating peroxides in solution.

HEXAGON DIGEST No. 17 (Jan. 1954)— Articles in this issue include *The Principles of Continuous Dyeing* by W. J. Marshall and R. W. Speke and *Some Aspects of the Electron Microscopy of Textile Fibres* by A. C. Cooper.

HEXAGON DIGEST No. 18 (April 1954)— This issue contains *The Dyeing of Cotton with Indigo* by J. T. Turner and *The Assessment of Whiteness in Paints* by D. Tough. The former describes past and present methods of applying indigo and contains a particularly interesting illustrated account of the primitive techniques still employed in China and the Near East.

HEXAGON DIGEST No. 19 (July 1954)— This issue contains *Investigations into the Dyeing of Hydrophobic Fibres. I— The Effect of Molecular Size and Dyeing Temperature* by T. Vickerstaff, *The Colour of Some Simple Anthraquinone Derivatives* by H. Sumner, and *The Measurement of Fibre Cohesion* by G. Grimshaw. The paper by Dr. Vickerstaff was read to the V.T.C.C. at Baden-Baden on 6th May 1954.

BRENTOSYN RB— This is a homogeneous coupling component recommended for use in conjunction with Dispersol Diazo Black B to give deep browns on Terylene staple fibre. The base and the coupling component are applied together from an aqueous dispersion in the presence of Tumescal D, and the colour is developed by simultaneous diazotisation and coupling in acidified sodium nitrite solution. A "reduction–clear" treatment is recommended after dyeing. Brentosyn RB is of no interest in conjunction with other bases and is of no value for dyeing other fibres. Fastness figures for a dyeing on Terylene slubbing using 6% of Brentosyn RB and Dispersol Diazo Black B include— Light 6–7, alkaline milling 5, repeated washing at 60°C. 5.

CARBINDONE PRINTING BLACK BS PASTE— This is a specially prepared and standardised paste form of the sulphur dye Carbindone Black B, and is of interest for giving deep blacks, of good fastness to light and washing on cellulosic materials, which are cheaper to produce than vat blacks. Since there is a considerable reduction in fastness with prints of pale to medium depth it is not recommended for greys. It may be printed alongside vat dyes and Alcian Blue 8G. Fastness figures on cotton include— Light 7, repeated severe washing (five times at 100°C.) 4, hypochlorite ("dry chemicking") 4–5.

CALEDON PAPER RED BNS POWDER FINE— This is a redispersible form of a red pigment suitable for dyeing paper in the beater. It has no affinity for cellulose and is only suitable for colouring sized papers; the dispersing agent present limits its use to the production of pale colours.

DYES FOR SEMI-CHROME GLOVING LEATHER— Dyeings of twenty Naphthalene Leather dyes and one Chlorazol Leather dye are included. The use of basic dyes for "topping" is essential on this type of tannage when full colours are required; a list of dyes suitable for this purpose is appended.

DYES FOR TERYLENE STAPLE FIBRE HALF HOSE— This card contains dyeings on hose panels knitted from 2/28s hosiery-twist Terylene staple fibre. Five disperse dyes are shown dyed both with and without Tumescal D, and also eight mixture dyeings of pale to medium depth. A further five heavy mixture dyeings, for the production of which a carrier is essential, are also shown. The scope of the "modified azoic technique" is illustrated by four dyeings based on Brentosyn BB and a selected disperse dye or Brentamine Fast Base.

DURANOL AND DISPERSOL DYES ON ACETATE RAYON— This card contains dyeings on acetate rayon cloth of 49 disperse dyes. With the exception of the navies and blacks, which are shown in two depths and a single depth respectively, three dyeings of each member are provided.

Data supplied include a comprehensive range of fastness figures and notes on particular characteristics and recommended uses, set out alongside the relevant patterns.

DURINDONE PRINTING MAGENTA BS PASTE— This vat dye is recommended for bright bluish reds of good fastness to light and hypochlorite on cellulosic fibres and is suitable for illuminated discharge styles. Fastness figures on cotton include— Light 4–5, washing (repeated severe, five times at 100°C.) 3–4, hypochlorite ("dry chemick") 5.

SOLEDON DYES ON VISCOSE RAYON STAPLE-FIBRE CLOTH— This card contains dyeings on spun rayon cloth of sixteen Soledon dyes. In addition to the usual fastness data details are given of the results obtained on cotton–viscose rayon mixture fabric when each dye is applied by a dyeing technique at particular temperatures and by padding.

Yorkshire Dyeware & Chemical Co. Ltd.

HEMASOL AR— This booklet describes methods of producing fast blacks on acetate rayon and nylon using Hemasol AR Paste, a specially prepared form of logwood. Details of the dyeing and fastness characteristics on these two fibres are given together with general methods of application on yarn and cloth supplemented with typical recipes. Additional information includes recommendations for dyeing mixture materials and for stripping dyed goods and identifying Hemasol-dyed acetate rayon and nylon. A short account is also given of some early experiences in jig dyeing acetate rayon and nylon with particular reference to faults and difficulties encountered and their elimination.

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., **68**, *23 (Jan. 1952), and also, together with symbols and the periodicals abstracted, in the annual index*

I—PLANT; MACHINERY; BUILDINGS

PATENTS

Colouring and Drying of Sheets of Paper, Cloth or the like. T. H. Burt. *BP* 715,964

The sheet is immersed in dye liquor and then spread on an inclined support. A carriage with a roller can be moved from one end of the support to the other so that excess dye liquid is squeezed out by the roller and runs down into a trough. C. O. C.

Dry Cleaning Machines. R. G. Whitaker and Universal Refrigerators. *BP* 715,833

Means for ensuring that thoroughly cleaned air enters the drum, for keeping the atmospheric temperature in the drum within desirable limits and for increasing solvent reclamation. C. O. C.

Dyehouse Truck. Alfred B. King Co. *USP* 2,649,965

The bottom of the truck slopes towards a small area at one side of it. A deflector directs the draining towards the point below the central portion of the body of the truck so that the liquid is not discharged close to the feet of the user. C. O. C.

Depositing Atomised Liquid Coatings. Harper J. Ransburg Co. *BP* 716,957

A method of obtaining improved uniformity in the thickness of coatings produced by annular sprays of coating composition deposited on moving surfaces. C. O. C.

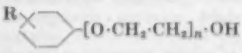
III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Non-ionic Surface-active Agents— Their Chemistry and Textile Uses. C. F. Jelinek and R. L. Mayhew. *Text. Research J.*, **24**, 765–778 (Aug. 1954).

Surface-active Agents in the Textile Industry. H. C. Borghetty. *Amer. Dyestuff Rep.*, **43**, P623–P627 (13 Sept. 1954).

Non-ionic Detergents. C F. Jelinek and R. L. Mayhew. *Ind. Eng. Chem.*, **46**, 1930–1934 (Sept. 1954).

Non-ionics mostly used in detergent compositions are— (*a*) ethylene oxide derivatives of alkylphenols—



($R = C_8$–C_{10} and $n = 8$–12); (*b*) ethylene oxide derivatives of tall oil, $R{\cdot}CO{\cdot}[O{\cdot}CH_2{\cdot}CH_2]_n{\cdot}OH$ ($n = 15$–18); and (*c*) alkanolamide (usually mono- and di-ethanolamine) derivatives of fatty acids. Whilst unbuilt oxyethylated detergents are superior in soil removal and whiteness retention to unbuilt anionics, the built non-ionics are only equal to built anionics. Built non-ionics are of value, however, where low foaming is required, as in automatic rotary washing machines. Alkanolamide derivatives are mainly used to improve the foam stability of anionics, with which they are mixed. Various specialised applications of non-ionic detergents are discussed. Improvements awaited are the development of a non-ionic formulation of high foam stability and the production of a solid non-ionic of high detergent power. W. K. R.

Factors limiting the Solubility of Non-ionic Detergents in Water. H. K. Livingston. *J. Colloid Sci.*, **9**, 365–368 (Aug. 1954).

Addition of phenols in amounts of the order of 1–10 g. per litre of non-ionic detergent solution lowers the temperature at which phase separation occurs by 5–50°C. pH appears to be an important factor affecting the solubility of non-ionic detergents. Some industrial applications utilising methods for decreasing the solubility of these non-ionic detergents are reviewed. W. R. M.

Building Synthetic Detergents. T. H. Vaughn, H. R. Suter, and M. G. Kramer. *Ind. Eng. Chem.*, **46**, 1934–1937 (Sept. 1954).

Various inorganic and organic builders are added to detergents to improve their performance. The function of builders in altering the physical and chemical properties of detergent solutions and the effect of such alterations in laundering are discussed. Currently used builders are classified and their main applications are indicated. W. K. R.

Molecularly Dehydrated Sodium Phosphates. B. C. Hafford. *Ind. Eng. Chem.*, **46**, 1938–1942 (Sept. 1954).

Pentasodium triphosphate, $Na_5P_3O_{10}$ (sodium tripolyphosphate), is the most important of the molecularly dehydrated sodium phosphates and is the predominant builder used in commercial (U.S.A.) synthetic detergent compositions, whilst tetrasodium pyrophosphate is used as a soap builder and sodium phosphate glasses (60–70% P_2O_5) are used in hard surface cleaning. They function as builders by their ability to improve soil removal, inhibit redeposition, sequester Ca and Mg ions, and deflocculate inorganic soils. Their corrosiveness towards certain metals can be inhibited. They are susceptible to hydrolytic decomposition in aqueous solution, but in most detergent applications the extent of such decomposition is negligible. W. K. R.

Production, Properties, and Uses of Fatty Alcohols. E. F. Hill, G. R. Wilson, and E. C. Steinle. *Ind. Eng. Chem.*, **46**, 1917–1921 (Sept. 1954).

Fatty alcohols are prepared by the reduction of fatty acids and esters and are used mainly in the form of sulphates as detergents. The two commercial methods of manufacture— sodium reduction and hydrogenation— are compared with respect to raw materials, plant construction, quality of product, and economics. Unsaturated alcohols are produced only by sodium reduction. Data are presented which indicate that the sulphates of unsaturated alcohols derived from tallow are superior to the sulphates of

saturated alcohols obtained by the hydrogenation of tallow, as detergent bases. Brief mention is made of other uses of fatty alcohols. W. K. R.

Alkylbenzenes. H. E. Bramston-Cook and W. E. Elwell. *Ind. Eng. Chem.*, **46**, 1922–1924 (Sept. 1954).

Alkylarylsulphonates are by far the most important class of anionic detergents [in the U.S.A.], and dodecylbenzenesulphonate is now used almost exclusively. The utility of alkylbenzenesulphonates for detergent applications depends on the nature and the molecular weight range and distribution of the alkyl group. The most suitable alkylbenzene is that prepared by condensing propylene tetramer with benzene; this has largely replaced "keryl"benzene, which is obtained by condensing with benzene an alkyl chloride derived from a C_{10-15} paraffin fraction. Brief descriptions are given of the methods of manufacture of both products. W. K. R.

Sulphonation of Alkylbenzenes. J. E. Kircher, E. L. Miller, and P. E. Geiser. *Ind. Eng. Chem.*, **46**, 1925–1930 (Sept. 1954).

A detailed description is given of the (batch) sulphonation of dodecyl(propylene tetramer)benzene with 20% oleum and a 3·2 : 1 mol. acid : hydrocarbon ratio at 77°F. The effect of process variables on the quality of the finished sulphonate is discussed. Methods of continuous sulphonation are described briefly. Sulphonation by means of stabilised sulphur trioxide, either by passing its vapour, diluted with N_2 or air, into the hydrocarbon, or by using liquid SO_2 as solvent, is shown to provide satisfactory products. W. K. R.

Some Applications of Organic *iso*Cyanates. G. S. J. White. *J.S.D.C.*, **70**, 481–486 (Nov. 1954).

The preparation, properties, and reactions of organic *iso*cyanates are touched upon. There follows a review of their uses as adhesives, in lacquers, and in textile finishing. Other developments mentioned include the manufacture of elastic and rigid sponges and rubbers. AUTHOR

PATENTS

Non-ionic Detergent. N. Salkin. *BP* 716,641

A mixture of a water-insoluble non-ionic detergent containing a short polyglycolether group of > 5 alkenoxy units and a water-soluble non-ionic dispersing agent or detergent containing a polyglycol ether group of < 6 alkenoxy groups has detergency superior to that of either of the components. C. O. C.

Substituted Carbamic Acid Esters as Surface Active Agents. Universal Oil Products Co. *USP* 2,649,473

Compounds of formula $HO(RO-)_xR^1{\cdot}NR^2{\cdot}C{\cdot}OR^3$ or $R^3R^2N{\cdot}C{\cdot}(OR^1)_xOH$ (R^1 = Alkylene of 2–5 C; R^2 = H, or subst. or unsubst. Alk; R^3 = Alk of 8–25 C; x = 2–25) have detergent and surface active properties. C. O. C.

Ethenoxy *N*-Monoethanolamides of Abietic Acid—Wetting and Detergent Agents. American Cyanamid Co. *BP* 716,128

The products obtained by heating monoethanolamine with abietic acid and then condensing with 8–50 mol. of ethylene oxide have good wetting and detergent properties for wool and cotton. C. O. C.

Mineral Oil Emulsions in Water. Svenska Oljeslageri. *BP* 717,119

Transparent emulsions which remain clear even when highly diluted are obtained by using at least half the weight of the oil of a product obtained by treating an alkanolamine-fatty acid condensate with an acid, e.g. the products described in *BP* 337,737, 306,116 and 337,774 (*J.S.D.C.*, **48**, 37 (1932); **47**, 43 (1931); **46**, 381 (1930). If such emulsions are used as spinning lubricants they are readily removed by water or weak alkali. C. O. C.

Size for Nylon Yarn. Monsanto. *USP* 2,651,587

An aqueous solution or dispersion of an ammonium, quaternary ammonium, sodium, potassium or other alkali salt of a styrene-alkylmaleate copolymer is an excellent size for nylon warps. C. O. C.

Fungicidal *cyclo*Hexadienone Derivatives. Basf. *BP* 716,020

Products having strong fungicidal activity are obtained by reacting hexachloro*cyclo*hexadiene-(1:4)-one(3) with compounds containing primary or secondary amino groups. C. O. C.

Rotproofing Solutions containing 40% of Copper. Phelps Dodge Corpn. *USP* 2,651,649

The product obtained by treating a xanthate and a sulphide, preferably in aqueous solution, with a salt or compound of copper contains 50% or more of copper and can be dissolved in hydrocarbon oils to yield solutions containing as much as 40% of copper. C. O. C.

Copper Diammonium Pentachlorophenolate. Dow Chemical Co. *USP* 2,651,648

Copper diammonium pentachlorophenolate, $Cu(NH_3)_2{\cdot}(C_6Cl_5O)_2$, is soluble in *cyclo*hexanone, methyl *n*-amyl ketone, Carbitol and butyl Carbitol and insoluble in water. It is used as a rotproofing agent for cellulose. C. O. C.

Tanning Agents. Firma Gustav Wurm, Lederfabrik. *BP* 716,664

The waste liquors obtained when wood from deciduous trees is digested contain substantial amounts of substances closely related to conventional natural tannin materials, e.g. syringic acid present in large quantity in the waste liquor from digesting beechwood with sulphite, is a dimethyl ether of gallic acid. An efficient method for the recovery of such substances is described. C. O. C.

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Annual Review of Unit Processes in Chemical Engineering. *Ind. Eng. Chem.*, **46**, 1785–1912 (Sept. 1954).

A comprehensive review of developments in 1953 contains *inter alia* sections dealing with—Amination by Reduction (17 references), Nitration (26 ref.), Polymerisation (468 ref.), and Sulphonation and Sulphation (464 ref.). W. K. R.

Historical Notes on the Wet-processing Industry. V—Sir William Perkin. S. M. Edelstein. *Amer. Dyestuff Rep.*, **43**, P 517–P 519, P 548 (16 Aug. 1954).

A. Poirrier 1832–1917. E. Justin-Mueller. *Teintex*, **19**, 685–695 (Sept. 1954).

A commercial and scientific biography of one of the pioneers of the French coal-tar dye industry, together with an appendix on the subsequent development to date of the Société des Matières Colorantes et Produits Chimiques de Saint-Denis. S. R. C.

Theory of Aromatic Substitution. IV—Orienting Influence of Substituents in Naphthalene Derivatives. F. L. J. Sixma. *Rec. Trav. chim.*, **73**, 235–242 (April 1954).

By means of calculations described elsewhere for estimating the inductive effect of substituents, it is shown that in electrophilic substitution reactions of naphthalene compounds a $+I$ substituent in position 1 or 2 directs further substitution mainly in position 5 with some taking place also in the 8 and 4 positions. A $-I$ substituent in position 1 directs the entering group into positions 4 and 8, whereas when it is in position 2 substitution takes place mainly in the 1 position.

Electrophilic substitution of 1-nitronaphthalene should be mainly in the 8 position, but a considerable amount of 5-substitution may be expected. This is in agreement with experimental results: e.g. nitration gives 64% 1:8- and 36% 1:5-dinitronaphthalene, chlorination gives mainly the 8-chloro derivative, but bromination gives mainly the 5-bromo compound. In the case of 2-nitronaphthalene, electrophilic substitution should be mainly in the 5-position, which also is in agreement with the experimental data: e.g. bromination gives mainly the 5-bromo derivative; nitration and sulphonation substitute mainly in the 5 and 8 positions. The theoretical positions of electrophilic substitution of dinitro- and trinitro-naphthalenes, which are also given, were found to be in agreement with experimental results. C. H. R.

Theory of Aromatic Substitution. V—Use of Hammett's Equation for the Correlation of Rates of Electrophilic and Nucleophilic Substitution Reactions. F. L. J. Sixma. *Rec. Trav. chim.*, **73**, 243–248 (April 1954).

By plotting the calculated localisation energies for a number of substituents for electrophilic reactions and for nucleophilic reactions against the localisation energies for side-chain reactions, it can be shown that where the substituent has an *I* effect the Hammett relation will hold with one set of σ-values for both side-chain and substitution reactions. In electrophilic reactions at the *para* position—*E* substituents may show some deviations, since the theory does not account for resonance interactions. The magnitude of the σ-values for electrophilic and nucleophilic substitution reactions in comparison with the values for side-chain reactions are in good agreement with the available experimental data. C. H. R.

Homolytic Aromatic Substitution. VI—Lead Tetrabenzoate—A New Phenylating Agent. D. H. Hey, C. J. M. Stirling, and G. H. Williams. *J.C.S.*, 2747–2751 (Aug. 1954).

Lead tetrabenzoate reacts with chlorobenzene and with nitrobenzene at 130°c. to give mixtures of the isomeric chlorodiphenyls and nitrodiphenyls respectively. The ratio of the isomers formed in the phenylation of nitrobenzene is similar to that with benzoyl peroxide as agent. Lead tetrabenzoate effects the fission of vicinal glycols, whereas with benzoyl peroxide oxidation to ketonic products results. The respective mechanisms are briefly discussed. H. H. H.

Oxidations with Phenyl Iodosoacetate. III—Primary Aromatic Amines in Acetic Acid. G. B. Barlin, K. H. Pausacker, and N. V. Riggs. *J.C.S.*, 3122–3125 (Sept. 1954).

Oxidation of a primary aromatic amine with phenyl iodosoacetate in acetic acid soln. generally gives the corresponding azo compound, although no identifiable oxidation product was obtained from aniline. β-Naphthylamine unexpectedly afforded 2-acetamido-1:4-naphthaquinone (up to 34%) and a cpd. $C_{32}H_{18}O_2N_2$ (25%), which is probably a β-naphthylamine anil of this quinone. *o*-Nitroamines do not yield the furazan oxides which are formed in high yields in benzene soln. (cf. *J.C.S.*, 1989 (1953)). H. H. H.

Reaction of Phenyl Iodosoacetate with *N*-Arylacetamides. G. B. Barlin and N. V. Riggs. *J.C.S.*, 3125–3128 (Sept. 1954).

Nitration of β-Nitronaphthalene. E. R. Ward and J. G. Hawkins. *J.C.S.*, 2975 (Aug. 1954).

Examination of the product obtained by nitration of β-nitronaphthalene in H_2SO_4 (sp. gr. 1·84) at 0°c. by means of its infrared absorption spectrum in the region 8–15 μ. established the presence of 1:6-(42 ± 5%), and 1:7-dinitronaphthalene (52 ± 5%) with 1:3:8-trinitronaphthalene (9 ± 5%). The product from similar nitration of α-nitronaphthalene contained 1:8-(69 ± 5%) and 1:5-dinitronaphthalene (31 ± 5% with some trinitronaphthalene). H. H. H.

Reactions of Aromatic Nitro Compounds with Alkaline Sulphides. V—2:3-, 2:6- and 1:7-Dinitronaphthalenes. E. R. Ward, T. M. Coulson, and J. G. Hawkins. *J.C.S.*, 2974–2975 (Aug. 1954).

The reduction of dinitronaphthalenes with almost neutral aq. CH_3OH–NaSH (cf. Hodgson and Ward, *J.C.S.*, 1187 (1949)) is now extended to the 2:3, 2:6, and 1:7 isomers. The results also show the abnormal behaviour of 1:3- and 1:8-dinitronaphthalene, which is accentuated by detailed comparison with the reactivity of 1:5-dinitro- and 1:3:8-trinitro-naphthalene. H. H. H.

Interaction of Polynitro Compounds with Aromatic Hydrocarbons and Bases. XII—Complexes of *N*-Alkylated Anilines with *s*-Trinitrobenzene and *s*-Trinitrotoluene. R. Foster and D. L. Hammick. *J.C.S.*, 2685–2692 (Aug. 1954).

The amounts of interaction between a nitro compound and members of homologous series are compared for the *N*-mono- and *NN*-di-*n*-alkylaniline series with *s*-trinitrobenzene and *s*-trinitrotoluene by means of association constants derived from colour measurements. For the higher members of both series, increased chain length results in complexes of greater stability. The wavelength of max. absorption due to the interaction rises with the first few members of both these series, thereafter remaining sensibly constant. The results are discussed mainly in the light of Mulliken's concept of charge-transfer complexes. H. H. H.

Reaction of Aromatic Amines with Acetylurethan. B. P. Bangdiwala and C. M. Desai. *J. Indian Chem. Soc.*, **31**, 50–52 (Jan. 1954).

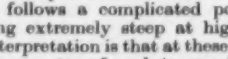
Aniline, *o*-, *m*-, and *p*-toluidine, and *o*- and *p*-anisidine and phenetidine gave with acetylurethan and $ZnCl_2$ at 150°c. corresponding symmetrical diarylureas. Aniline and acetylurethan with $ZnCl_2$ or $HgCl_2$ at 95–100°c. gave the corresponding metal chloride–anil complex, from which the free anil could not be isolated. Aniline, acetylurethan, and PCl_3 in toluene gave the symmetrical diarylurea and acetylphenylurea ($C_6H_5{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CH_3$). *s*-Diarylureas were obtained from the corresponding acetylarylureas by heating with dilute sulphuric acid on a steam bath. C. H. R.

Kinetics of the Reduction by Titanous Chloride of Azobenzene and 4-Aminoazobenzene. N. R. Large, F. J. Stubbs, and C. Hinshelwood. *J.C.S.*, 2736–2743 (Aug. 1954).

Reduction of *trans*-azobenzene or of *trans*-4-aminoazobenzene by $TiCl_3$ in aq. alcoholic soln. is of the first order with respect to each component, the rate-determining step being the transfer of an electron from a titanous species to the azo cpd. which has taken up protons. (The *cis*-compounds are reduced with very great rapidity.) The 4-amino cpd. yields aniline and *p*-phenylenediamine, but the unsubstituted azo cpd. gives hydrazobenzene, 84% of which is very rapidly transformed into benzidine (or isomers), the remainder suffering reduction or disproportionation. The most remarkable characteristic of the reductions is their dependence on the concn. of HCl and of Cl-ions, which follows a complicated power series, the curves becoming extremely steep at higher acid concn. The simplest interpretation is that at these concn. electrons from the $TiCl_3$ are transferred to species of the type $C_6H_5{\cdot}N^+H{:}N^+H{\cdot}C_6H_5$, the formation of which is facilitated by the screening action of oppositely charged Cl-ions. Analogous assumptions about proton addition to azo or hydrazo cpd. are useful in explaining the benzidine transformation and the disproportionation or reduction reactions. H. H. H.

Carcinogenic Azo Compounds. G. M. Badger, G. E. Lewis, and R. T. W. Reid. *Nature*, **173**, 313–314 (13 Feb. 1954).

2:2′-Azonaphthalene (I) and compounds of structure—



(X and Y = H, O·CH_3, or N(CH_3)$_2$) were tested for carcinogenic activity in rats maintained on a controlled diet. Activity appears to be associated with (*a*) presence of an amino group, and (*b*) optimum electron density around the azo linkage. Thus I and 4-methoxy- and 4:4′-dimethoxy-azobenzene were inactive; 4′-methoxy-4-dimethylaminoazobenzene was moderately active; 4-dimethylaminoazobenzene was highly active; whilst 4:4′-bisdimethylaminoazobenzene showed no activity. E. S.

Organic Pigments. IV—Synthesis of Benzidine Yellows. E. Koike, S. Suzuki, and I. Tanakadate. *Rept. Govt. Chem. Ind. Research Inst. Tokyo*, **49**, 147–152 (1954); **V—Pigments derived from 1-Phenyl-3-methyl-5-pyrazolone.** E. Koike, S. Suzuki, I. Tanakadate, H. Iida, and M. Okawa. *Ibid.*, 153–157; **VI—Synthesis of Pyrazolone Reds.** E. Koike, S. Suzuki, I. Tanakadate, and H. Iida. *Ibid.*, 158–163: *Chem. Abs.*, **48**, 11078 (25 Sept. 1954).

IV—Benzidine and its homologues were tetrazotised with 35% HCl* and $NaNO_2$ at 0–3°c. and then coupled with acetoacetanilide and its homologues at 0–2°c. in weak acid or alkali to yield yellows whose fastness to light increased when the diazo components contained an electro negative substituent, e.g. Cl, but decreased when the substituent was electro positive, e.g. CH_3 or OCH_3, and/or when that in the coupler was electro negative, e.g. Cl or NO_2, correlating with Hammett's substitution constants obtained in C_6H_5COOH.

*Probably 35% HCl was used as a reagent.

V— 3:3′-Dichlorobenzidine was similarly tetrazotised and then coupled with 1-phenyl-3-methyl-5-pyrazolone to yield an orange pigment of good fastness to light. The hue shifted toward red with substitution of NO_2 at the *p*-position and toward yellow progressively with OCH_3, CH_3, Cl and SO_3Na in that order. Fastness to light of these orange pigments changed similarly to that of the benzidine yellows.

VI— 3:3′-Dichlorobenzidine was similarly tetrazotised and coupled with 1-phenyl-3-(carboxyethyl)-5-pyrazolone to yield a red pigment fast to light and oil. Hue was affected more by substitution in the pyrazolone ring than in the phenyl component. Fastness to light increased with greater difference in electron density on the two sides of the azo bridge. C. O. C.

Azo Derivatives of Thiazole. G. Modena and A. Risalti. *Boll. Sci. Fac. Chim. ind. Bologna*, **11**, 65–69 (1953); G. Modena and L. Pentimalli. *Ibid.*, **11**, 70–72 (1953): *Chem. Abs.*, **48**, 9065 (10 Aug. 1954).

Various 2-aminothiazoles, 2-aminobenzothiazoles, and 2-aminonaphthothiazoles were diazotised and coupled with dimethyl(and diethyl)aniline, *α*- and *β*-naphthylamine, H acid, and Schaeffer's acid, and m.p. and absorption data recorded. E. S.

***N*-Acyl Dyes derived from 3-Sulpho-7-amino-8-(2-sulpho-4-aminophenylazo)-1-naphthol.** I. Okubo and T. Kitagawa. *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **56**, 344–346 (1953): *Chem. Abs.*, **48**, 10646 (25 Sept. 1954).

Nine 4′-acylamino derivatives of 3-sulpho-7-amino-8-(2′-sulpho-4′-aminophenylazo)-1-naphthol disodium salt (I) were prepared. They had the structures: $RCOCH_3$, $RCOC_6H_{11-8}$, $RCOC_6H_5$, $RCOCH{:}CHC_6H_5$, $RCOCH_2Cl$, $RCO(CH_2)_4COR$, $RCO(CH_2)_4COR$, RCOCOR and RCOR (R = nucleus of I). The absorption spectra of their aqueous solutions showed that the maximum absorption range is 500–530 m*μ*. The spectral reflection curves of fibres dyed with these compounds show that the principle reflection is 493–496 m*μ*. (illumination C, C.I.C. method). Monoazo derivatives have especial affinity for wool. The effects of acyl hypsochromes are briefly discussed. C. O. C.

Action of Light on Some Organic Colouring Matter— III. C. M. Desai and B. K. Vaidya, *J. Indian Chem. Soc.*, **31**, 389–392 (May 1954).

The rate of fading of solutions of Crystal Violet, Malachite Green, Rosaniline, Brilliant Green, Naphthol Yellow, Chrysoidine, aminoazobenzene, and picric acid on exposure to a mercury arc lamp, a Point-o-lite lamp, and sunlight have been measured by colorimetric comparison of the faded solutions with an unfaded solution in the Leitz colorimeter. The first four dyes gave linear rates of fading with all three light sources. Aminoazobenzene and Chrysoidine gave parabolic rates, i.e. $x \propto t^{\frac{1}{2}}$ where x = concn. faded in time t. With Naphthol Yellow and picric acid, linear rates were obtained with the mercury lamp, but with the other light sources the rate changes from linear to parabolic after 50% and 80% respectively of the dye has faded. A. J.

Dark and Photochemical Reactions of Oxygen and Moisture with Triphenylmethane Dyes in the form of Films. I. I. Dilung and B. Ya. Dain. *Doklady Akad. Nauk S.S.S.R.*, **95**, 1001–1004 (11 April 1954).

Films of dye (Crystal Violet, Malachite Green) are prepared by pouring a conc. alcoholic soln. of the dye on to a clean glass plate and causing the solvent to evaporate rapidly. The absorption spectra of the films differ appreciably from those of alcoholic soln. of the dyes. For example, Crystal Violet in soln. has an absorption max. at 590 m*μ*., and an inflection in the curve indicates that there is a component band having a max. at ~ 540 m*μ*. The film, however, has its principal max. at 540 m*μ*., and the presence of the 590 m*μ* max. is indicated only by a slight inflection. When the film is subjected to a high vacuum at 70°c., the absorption spectrum changes considerably (broader band, principal max. at 575 m*μ*., indications of second max. at ~ 640 m*μ*.). Admission of dry air does not affect the spectrum, but admission of moisture causes it to revert immediately to its original form. This movement of the band to shorter waves is to be associated with combination of dye with water under adsorption conditions (only feeble indications of such short-wave bands are to be found in aq. soln.). When the film is irradiated with visible light (1000-watt lamp), fading is rapid, and it cannot be effectively checked by the above evacuation treatment. However, after removal of all traces of oxygen (many repetitions of the sequence— admission of pure nitrogen, evacuation, degassing at 80–90°c.), a state of stability to light is ultimately reached, and this state is unaffected by admission of moisture (free from oxygen). Presence of oxygen, therefore, is essential for the occurrence of fading, and the changes occurring in the absorption spectrum during fading in a normal atmosphere indicate that photochemical oxidation of the dye–water complex (photoactivation of the complex, which enables it to pass an electron to an oxygen molecule) is the dominant process, although attack on non-hydrated dye may be appreciable under conditions that do not permit the ready formation of new dye–water complexes. The behaviour of Malachite Green is quite analogous to that of Crystal Violet. A. E. S.

Effect of Fuchsin Red on the Metabolism of Yeasts. K. Bahadur. *Bull. Chem. Soc. Japan*, **27**, 297–300 (July 1954).

The effect of selective light absorption on the metabolism of yeasts was studied by adding various amounts of Fuchsin Red to the cultures. The hindrance to growth was proportional to the amount of dye in the culture. W. K. R.

Reaction between Acridine and Methyl Acetylenedicarboxylate. R. M. Acheson and M. L. Burstall. *J.C.S.*, 3240–3245 (Sept. 1954).

In methanol the reaction between acridine and methyl acetylenedicarboxylate affords mainly the bright red 10-(*trans*-1 : 2-dimethoxycarbonylvinyl)acridinium methoxide, but in ether methyl 5:10-dihydro-5-oxoacridinyl-fumarate and -maleate are formed. Hydrogenolysis of the fumarate gives acridone and methyl fumarate. H. H. H.

Cyanine Dyes.— IV. H. Zenno. *J. Soc. Sci. Phot. Japan*, **15**, 99–108 (1953): *Chem. Abs.*, **48**, 11063 (25 Sept. 1954).

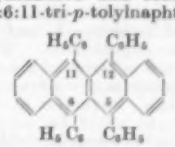
An account of experiments on the synthesis of *mero*-carbocyanines and polymethincyanines from quaternary salts containing a reactive methyl group and the sodium salt of formylacetophenone. C. O. C.

Dimroth's Alleged *ortho*Naphthazarin. J. Garden and R. H. Thomson. *Chem. and Ind.*, 1146–1147 (11 Sept. 1954).

The preparation by Dimroth and Roos of what they believed to be 5:6-dihydroxy-1:4-naphthaquinone (*ortho*-naphthazarin) (*Liebigs Annalen*, **456**, 177 (1927)) has been reinvestigated; the resulting cpd. differs from that described by Dimroth and Roos (I) only in that it contains N. It is believed that I is 5-amino-6-hydroxy-1:4-naphthaquinone, and that this explains the apparently anomalous behaviour of the acetyl and benzoyl derivatives: these undergo 6- to 5-position rearrangements, for which analogies are well known. J. W. D.

Substituted Anthracene Derivatives. VII— Some Naphthacene *endo*Oxide Derivatives. C. M. Badger, R. S. Pearce, H. J. Rodda, and I. S. Walker. *J.C.S.*, 3151–3160 (Sept. 1954).

The original rubrene skeleton (I) is retained in rubrene mono-oxide (II) but not in rubrene *iso*-oxide, for which structure III is proposed. Tetra-*p*-tolylnaphthacene *iso*-oxide ("tetramethylrubrene *iso*-oxide") has been synthesised and reduced with Mg and $CH_3{\cdot}MgI$ to 5:6:11-tri-*p*-tolylnaphthacene and *p*-cresol.



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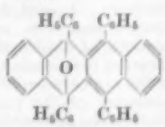

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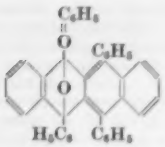


(III)

H. H. H.

Substituted Anthracene Derivatives. VIII— The Conjugating Powers of the Substitution Positions in 3:4-Benzophenanthrene. G. M. Badger and I. S. Walker, *J.C.S.*, 3238–3240 (Sept. 1954).

The absorption spectra of 3:4-benzophenanthrene (I) and of its six monomethyl deriv. show that the bathochromic shift produced by methyl substitution is greatest at the 5-position, and that, in agreement with theory, the 2- and 8-positions have greater conjugating powers than the 6- and 7-positions. The anomaly in the case of 5-substitution is associated with the non-coplanarity of the methyl group.

(I)

H. H. H.

Prediction of the Reactivity of some Penta- and Hexa-cyclic Hydrocarbons. P. H. Gore. *J.C.S.*, 3166–3168 (Sept. 1954).

Dewar's simplified molecular-orbital treatment (cf. *J. Amer. Chem. Soc.*, **74**, 3357 (1952)) is applied to more complex polycyclic hydrocarbons, viz. anthanthrene, the five dibenzophenanthrenes, the five dibenzopyrenes, and zethrene. Results obtained are correlated with the geometry of the systems. The abnormal acidity of 1:2-6:7-dibenzopyren-3-ol and the structure of the cation formed by zethrene in acid media are discussed. H. H. H.

Synthesis of Benzanthrone and Dyes derived from it. IV— Halogenation of *iso*Dibenzopyrenequinone. E. Chubachi, I. Tamakadate, and T. Kaneko. *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **56**, 339–341 (1953); **V— Condensation of Benzanthrone with Amino Compounds.** *Ibid.*, 341–344: *Chem. Abs.*, **48**, 10711 (25 Sept. 1954).

IV— *iso*Dibenzopyrenequinone was chlorinated with SO_2Cl_2 in nitrobenzene, and brominated by Br in a mixture of conc. H_2SO_4 and $ClSO_3H$. The colour of the products was examined by a spectrophotometer. Introduction of up to 3 Cl atoms per molecule improves the dyeing property, but produces an orange-yellow dye. The brominated product is a dark red dye of dyeing properties similar to the original compound. Fastness to light was not affected by halogenation.

V—Properties of various dyes formed by treating benzanthrone with various amino compounds, e.g. *a*-aminoanthraquinone, are described. A violet-grey vat dye was obtained by stirring the condensation product of benzanthrone and *a*-aminoanthraquinone, in $ClSO_3H$ for 3–5 hr. at 70°c. C. O. C.

Phosphorescence Spectra of Naphthalene and Some Simple Derivatives. J. Ferguson, T. Iredale, and J. A. Taylor. *J.C.S.*, 3160–3165 (Sept. 1954).

A photomultiplier technique is used to measure the phosphorescence emission from naphthalene and 1:5-dideutero-, 1- and 2-fluoro-, 1- and 2-chloro-, 1- and 2-bromo-, and 1:5- and 2:6-dibromo-naphthalene. The spectrum of naphthalene is interpreted in terms of known vibration frequencies, and an explanation is now advanced for the appearance of *b*,*g* fundamentals. Reduction in the symmetry of the parent mol. brought about by simple substitution causes marked changes in the spectrum, which are explained in some detail. H. H. H.

Synthesis of Organic Fluorescent Compounds. XXIII— Synthesis of 9-Carboxymethyl-3:6-diaminocarbazole-4:4-disulphonic Acid and its Fluorescence. Z. Yoshida and R. Oda. *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **56**, 261–263 (1953); **XXIV— Syntheses of 9-Carboxymethyl-3:6-bis[(4-hydroxy-6-substituted-2-*s*-triazyl) amino] carbazole-4:4-disulphonic Acid.** Z. Yoshida, Y. Kato, and R. Oda. *Ibid.*, 346–348: *Chem. Abs.*, **48**, 10748 (25 Sept. 1954).

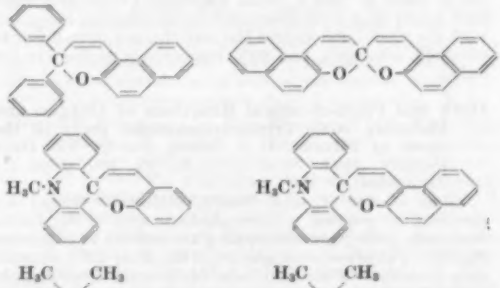
XXIII— The fluorescence of 3:6-diaminocarbazole-4:4-disulphonic acid* tends to fade on exposure to light because of oxidation and sensitisation. To get an improved product the foregoing* (0·28 mol.) was treated with HCHO (0·42), $NaHSO_3$ (0·45) and KCN (0·42) in aq. soln. to yield 79·5% of 9-carboxymethyl-3:6-dinitrocarbazole-4:4-disulphonic acid. This was treated with Fe powder and acetic acid at 95–97°c. for 2 hr. to yield 75% yellow crystals of 9-carboxymethyl-3:6-diaminocarbazole-4:4-disulphonic acid which showed strong, stable bluish green fluorescence in aq. soln. at pH 2·2–1·2.

*The above information is correctly transcribed from *Chem. Abs.*, but the numbering "4 : 4-disulphonic", which occurs throughout, is clearly incorrect; and the word "foregoing" must be understood as referring to the 3 : 6-dinitro cpd. corresponding to the "foregoing".

XXIV—9-Carboxymethyl-3:6-diaminocarbazole-4:4-disulphonic acid (0·01 mol.) was treated with cyanuryl-chloride (0·02) at 0°c. and pH 6·5, filtered, the filtrate treated for 2·5 hr. with various amines (usually 0·02 mol.) at 35–40°c. and pH 6·5, stirred 2 hr. at 90°c., salted out, filtered, washed with water, and recrystallised. The following compounds were produced (the substituent in the 6′ and 6″ position given): $N(CH_3)_2$, $N(C_2H_5)_2$, $NH(CH_2)_2OH$, NHC_6H_5, $NHC_6H_4SO_3Na$-*p*, NHC_6H_4COONa-*o*, NHC_6H_4COONa-*p*, $NHC_6H_4CH_3$-*o*, $NHC_6H_4OCH_3$-*o*, $NHC_6H_4OCH_3$-*p*. The blue to bluish-violet fluorescence of these compounds under a mercury lamp was stronger than that of 3:6-diaminocarbazole-4:4-disulphonic acid described in the preceding paper. C. O. C.

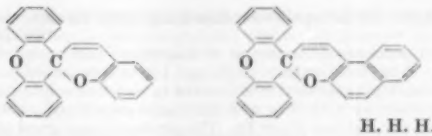
Photochromism and Reversible Multiple Internal Transitions in some *spiro*Pyrans at Low Temperatures— II. Y. Hirshberg and E. Fischer. *J.C.S.*, 3129–3137 (Sept. 1954).

Previous investigations (cf. *J.C.S.*, 297 (1954)) are now extended to the 8 types of cpd. below. Under appropriate conditions each photochromic cpd. gives rise to one or more coloured modifications, all of which spontaneously revert to the original colourless modification at rates depending on temp. Thermochromic and photochromic absorption spectra are recorded and compared; heats of interconversion are estimated. In several cases the colour of the dyes formed by ultraviolet irradiation at low temp. is found to depend reversibly on the temp. of measurement. It is suggested that the various coloured modifications are stereoisomers.



R = R′ = H
R = R′ = O·CH$_3$
R = H, R′ = O·CH$_3$
R = O·CH$_3$, R′ = H

R = H
R = O·CH$_3$



H. H. H.

Azulenes and Related Substances. V— *cyclo*-Pentenocycloheptan-4-one. S. Dev. *J. Indian Chem. Soc.*, **31**, 1–7 (Jan. 1954).

Comparison of some Natural and Synthetic Melanins. W. D. Stein. *Nature*, **174**, 601–602 (25 Sept. 1954).

Ultraviolet absorption spectroscopic studies are reported, the results of which suggest that certain natural and synthetically prepared melanins are similar in structure.

J. W. D.

Researches on Polyenes. I— Synthesis of Corticrocin. B. L. Shaw and M. C. Whiting. *J.C.S.*, 3217–3221 (Sept. 1954).

The constitution HOOC·[CH:CH]$_4$·COOH, proposed for the fungus pigment corticrocin by Erdtman (*Acta Chem. Scand.*, **2**, 209 (1948)), is now confirmed by synthesis.

H. H. H.

Structure of αω-Diphenylpolyenes. W. Drenth. *Rec. Trav. chim.*, **73**, 249–263 (April 1954).

The bond lengths, resonance energies, frequency of the first ultraviolet absorption, and probability of transition for this band have been calculated to a first approximation by the method of linear combination of atomic orbitals–molecular orbitals (LCAO–MO) for the compounds C_6H_5·[CH:CH]$_n$·C_6H_5 (n = 0–5). For compounds in which n = 0–2 the calculations were extended to a second approximation.

C. H. R.

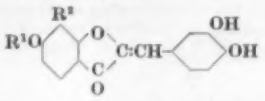
Survey of Anthoxanthins. VI— Colouring Matter of *Tamarix troupii*. Constitution of the Aglycone and its Synthesis. S. R. Gupta and T. R. Seshadri. *J.C.S.*, 3063–3065 (Sept. 1954).

The green leaves of *Tamarix troupii* contain a glycoside, tamarixin, of a new flavonol, whose constitution is now established synthetically as 3:5:7:3′-tetrahydroxy-4′-methoxyflavone.

H. H. H.

Anthochlor Pigments. IX— Structure of the Aurone Pigment of *Cosmos sulphureus*, "Orange Flare" and "Yellow Flare". T. A. Geissman and L. Jurd. *J. Amer. Chem. Soc.*, **76**, 4475–4476 (5 Sept. 1954).

The aurone pigment sulphuretin isolated from the orange and yellow forms of the flowers of *C. sulphureus*, its glucoside, and leptosin are all of formula—



Sulphuretin	...	$R^1 = R^2 = H$
Sulphurein	...	R^1 = glucosyl, $R^2 = H$
Leptosin	...	R^1 = glucosyl, $R^2 = OCH_3$.

C. O. C.

Dyes, Aromatics, Antibiotics, and Narcotics from Lichens living on Trees. H. Gams. *Österr. Apoth.-Ztg.*, **8**, 439–441 (1954): *Chem. Abs.*, **48**, 10955 (25 Sept. 1954).

Review, 36 references.

C. O. C.

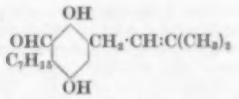
Actinomycete Pigments. II— Limocrocine, a Yellow Actinomycete Pigment. H. Brockmann and G. Grothe. *Chem. Ber.*, **86**, 1110–1115 (1953): *Chem. Abs.*, **48**, 10686 (25 Sept. 1954).

A crystalline yellow dye, limocrocine, $C_{50}H_{56}O_5N_2$, is obtained from the culture solution of *Streptomyces limosus*, owes its colour to a system of conjugated aliphatic double bonds, it is therefore a polyene dye.

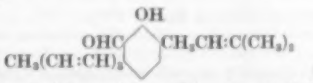
C. O. C.

Structure of Flavoglaucin and Auroglaucin. A. Quilico, C. Cardani, and L. Panizzi. *Atti Accad. nazl. Lincei Rend., Classe Sci. fis., mat., e nat.*, **14**, 358–364 (1953): *Chem. Abs.*, **48**, 10663 (25 Sept. 1954).

Evidence is given to show that the pigment of the mould *Aspergillus glaucus* is 2-*iso*pentenyl-5-*n*-heptyl-6-gentisaldehyde—



and not 2-*iso*pentenyl-5-*n*-heptyl-6-methylquinol as suggested by previous workers. Auroglaucin has the structure—



C. O. C.

Chemistry of Bacteria. III— An Indolylpyrrylmethene from Violacein. R. J. S. Beer, B. E. Jennings, and A. Robertson. *J.C.S.*, 2679–2685 (Aug. 1954).

Degradation of acetylviolacein with HI gives a yellow mono-acidic base $C_{13}H_{10}O_2N_2$, which forms a deep red monohydrochloride and perchlorate and appears to be a 5-hydroxyindolyl-hydroxypyrrylmethene. It is inferred from the properties of synthetic model compounds that this type of system is also present in violacein.

H. H. H.

Cadmium Pigments. P. J. Curtis and R. B. Wright. *J. Oil and Col. Chem. Assocn.*, **37**, 26–43 (Jan. 1954).

Pigments derived from cadmium sulphide, cadmium sulphoselenides, and coprecipitants are described. Methods of manufacture are outlined, and data given on both qualitative and quantitative analytical methods, colour, and particle size distribution. The uses of these pigments in paints, artists' colours, rubber, plastics, printing inks, wallpaper, leather, glass, and vitreous enamels are briefly discussed.

C. J. W. H.

Composition of Berlin Green (Ferric Ferricyanide)— Conductometric Studies. R. S. Saxena and A. K. Bhattacharya. *J. Indian Chem. Soc.*, **31**, 53–55 (Jan. 1954).

The composition of Berlin Green is shown to be ferric ferricyanide ($Fe^{3+}[Fe^{3+}(CN)_6]$) by conductometric titrations between ferric chloride and potassium ferricyanide at several concentrations. The slight discrepancies between the calculated and experimental values can be explained by the adsorption of Fe^{3+} and $Fe(CN)_6^{3-}$ ions by the precipitated complex. These results are in agreement with those obtained by thermometric investigations.

C. H. R.

Spinel Pigments. G. Yamaguchi, H. Tanabe, and K. Tomiura. *J. Ceram. Assocn. Japan*, **62**, 191–196 (1954): *Chem. Abs.*, **48**, 11023, (25 Sept. 1954).

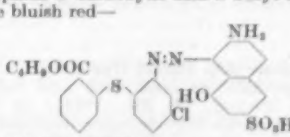
Pigments of the following systems and compounds were prepared CoO–MgO–Al_2O_3 blue, CoO–NiO–MgO–Al_2O_3 blue, NiO–Al_2O_3 blue, CuO–Al_2O_3 brown, CoO–MgO–$2Cr_2O_3$ green, CoO–ZnO–$2Cr_2O_3$ green, CoO–$3MgO$–$2Cr_2O_3$–$2Al_2O_3$ green, NiO–MgO–CoO–SnO_2 blue, NiO–CoO–ZnO–SnO_2 green, ZnO–Cr_2O_3–Al_2O_3 pink, MgO–Cr_2O_3–Al_2O_3 brown. In the last four systems pigments containing MgO were unstable. CuO–Al_2O_3 was brown at 750°c. and became blue at 1100°c. when the spinel structure was lost.

C. O. C.

PATENTS

Red Monoazo Acid Dyes from *o*-Aminodiphenyl Sulphides. Gy. *BP* 715,549

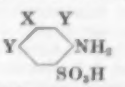
Monoazo dyes which dye wool red from a neutral or weakly acid bath are made by diazotising an *o*-aminodiphenyl sulphide free of solubilising groups and acid-coupling with γ acid. Thus from 2-amino-4-chlorodiphenyl sulphide 2′-carboxylic acid *n*-butyl ester there is obtained the bluish red—



E. S.

Monoazo Acid Orange Dyes. S. *BP* 716,007

Diazotised orthanilic acid or its derivatives—

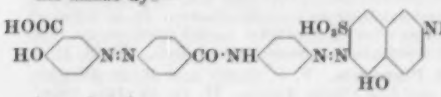


(X = H or other substituent other than NO_2, SO_3H, or COOH; Y = H or Alk, or if one Y = H the other Y may

be joined to position X by the chain $-CH_2\cdot CH_2\cdot CH_2\cdot CH_2-$) coupled with an *N*-acyl-J acid in which the acyl group has 8–12C gives orange acid dyes, of better wash-fastness than the similar dyes of *BP* 432,020 (J.S.D.C., **51**, 396 (1935)) which have an *N*-acyl group of < 4C. Thus the monoazo compound orthanilic acid→*N*-octanoyl-J acid dyes wool, silk, and nylon bright orange from a weakly acid bath. E. S.

Disazo Direct Cotton Reds. FBy. *BP* 716,001

Tetrazotised 4-amino-*p*-aminobenzanilide coupled with 1 mol. of an aromatic *o*-hydroxycarboxylic acid and 1 mol. of *N*-acetyl-J acid gives red direct cotton dyes superior in hue, affinity and cellulose acetate reserve properties to the similar dyes of *BP* 584,838 (J.S.D.C., **63**, 192 (1947)) in which *N*-benzoyl-J acid is used in place of *N*-acetyl-J acid. Thus by coupling first with 1 mol. of salicylic acid in presence of Na_2CO_3 and then, after making just acid with HCl, with 1 mol. of *N*-acetyl-J acid in presence of $NaHCO_3$, the disazo dye—



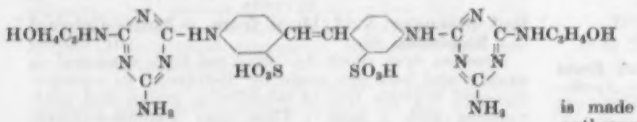
is produced. E. S.

Dischargeable Stilbene Azo Direct Cotton Oranges. FBy. *BP* 715,715

The condensation of 4:4′-dinitrostilbene-2:2′-disulphonic acid or 4:4′-dinitrodibenzyl-2:2′-disulphonic acid with aminoazo compounds in presence of NaOH in each case yields two main constituents, one dischargeable and the other not dischargeable. By increasing the amount of aminoazo compound present from 1 mol. to ca. 1·6–2 mol. added at intervals during the condensation, and increasing the condensation time to 20–30 hr., the proportion of dischargeable component is increased. It may be separated from the non-dischargeable component by taking advantage of the difference in solubility of the hydrazoazo compounds formed by mild reduction. Thus to sodium 4-aminoazobenzene-4′-sulphonate (29·9 parts) dissolved in boiling aq. NaOH is added over 2 hr. 4:4′-dinitrostilbene-2:2′-disulphonic acid (28·5 parts), and heating is continued a further 20 hr. Dextrose and aq. NaOH are added at 70°c. followed by salt, and the mixture is filtered. Air is blown through the filtrate to precipitate the yellowish orange dischargeable direct cotton dye. E. S.

Diaminostilbene Triazines— Fluorescent Whitening Agents. FBy. *BP* 715,239

Fluorescent whitening agents of good light fastness are prepared by treating a suspension of cyanuric chloride in acetone with an aq. soln. of the Na salt of 4:4′-diaminostilbene-2:2′-disulphonic acid at 5°c., neutralising with Na_2CO_3 and adding monoethanolamine with aq. Na_2CO_3 at 40°c. followed by aq. NH_3 at 80–85°c. Acidifying precipitates the compound—



which is converted to its NH_4 or alkali metal salt. R. K. F.

Anthraquinone-Azo Direct Dyes. S. *BP* 713,580

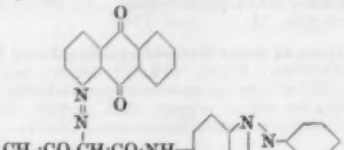
The terephthalic or *iso*phthalic acid halide used in *BP* 554,463 (J.S.D.C., **59**, 256 (1943)) to link a blue aminoanthraquinone with a yellow aminoazo compound is replaced by a dicarboxylic halide of general formula—

$$Hal\text{–}CO\text{–}CH{=}CH\text{–}CO\text{–}Hal$$

where one H may be substituted by Cl, Br or CH_3. The resulting green dyes are highly substantive. Thus the condensation product of 1-amino-4-bromoanthraquinone-2-sulphonic acid and 4:4′-diamino-1:1′-diphenyl-3-sulphonic acid, and 4-aminoazobenzene-4′-sulphonic acid are treated in aq. soln. at 0–3°c. with fumaryl chloride while maintaining at pH 4·5–5·0 by adding NaOH. R. K. F.

Leuco Anthraquinone-Azo Sulphuric Esters. DH. *BP* 715,039

1-Aminoanthraquinone is diazotised and coupled with a 5-acylacetylamino-2-phenyl-1:3-benzotriazole. The resulting compound is converted to its leuco sulphuric ester by treating with SO_3, or a substance capable of yielding it, and a metal, e.g. Cu or Fe. The products have good affinity for cellulose and give fast yellow dyeings on oxidising. Thus the dye—



is treated with $ClSO_3H$ and Fe powder in pyridine at 50°c. for several hr. The product is separated by pouring into aq. Na_2CO_3, removing the pyridine by vacuum distillation, screening and adding NaCl. R. K. F.

***leuco*-Indanthrone Sulphuric Esters.** American Cyanamid Co. *BP* 715,738

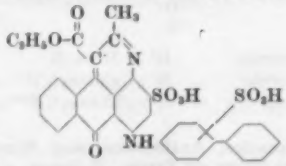
The *leuco*-sulphuric ester of a *β*-aminoanthraquinone having a free position *α* to the NH_2 group is oxidised with a compound of Co or Ni in the tri- or tetra-valent state, or of Fe in the tetra- or hexa-valent state. Thus, cobaltic hydroxide, prepared by treating aq. cobaltous acetate with KOH and NaOCl, is added to an aq. soln. of 2-amino-3-chloroanthraquinone-9:10-disulphuric ester (hydrolysis of the corresponding acetylamino derivative with NaOH) at 85°c. R. K. F.

Sulphur-containing Vat Dyes. CFM. *BP* 715,767

The reaction products of glyoxal and anthrones described in *BP* 299,972 (J.S.D.C., **45**, 89 (1929)) are treated with sulphur or a sulphur compound in presence of a Friedel-Craft condensing agent, e.g. $AlCl_3$, to produce non-tendering olive to green sulphur-containing vat dyes. Thus, the red-violet dye of *BP* 299,972 is stirred with $AlCl_3$, $SOCl_2$ and S_2Cl_2 at 20–25°c. The product is separated by pouring on to ice. R. K. F.

Anthrapyridine Derivatives— Acid Dyes. S. *BP* 715,241

1-Aminoanthraquinones which may be substituted in the 2-position with Cl, Br, Alk or SO_3H; and in the 4-position with Cl, Br, NO_2, OCH_3, or NHAryl, are treated under acid conditions with an alkyl ester of acetoacetic acid to produce the corresponding anthrapyridine carboxy ester. The products are yellow to red acid dyes, which are further sulphonated if necessary. Thus the red dye—



is made by heating 1-amino-4-(*p*-phenyl)phenylamino-anthraquinone-2-sulphonic acid with ethyl acetoacetate in nitrobenzene at 160°c., while removing volatile reaction products by passing air; separating by adding chlorobenzene and Na_2CO_3 and further sulphonating in H_2SO_4 at 20°c. R. K. F.

Phthalocyanine Preparation. General Aniline. *BP* 714,083

The preparation of phthalocyanines by condensing phthalic anhydride or related substances with urea and a metal-yielding compound in an inert solvent, is carried out in the presence of < 25% of the weight of the anhydride of an alkali metal or alkaline earth metal phosphate. Thus, phthalic anhydride, urea, ammonium molybdate NaH_2PO_4 and $AlCl_3$ are refluxed (200–205°c.) in trichlorobenzene for 6 hr. More urea in trichlorobenzene is then added and heating continued for a further 5 hr. An 85% yield of pure chloroaluminium phthalocyanine is obtained. R. K. F.

Dispersible β-Phthalocyanines. Ciba. *BP* 715,763

Dispersible β-phthalocyanines which are greener than the corresponding α-forms are prepared by grinding the crude phthalocyanine in e.g. a rod mill with a water sol. grinding substratum, e.g. anhyd. Na ferrocyanide, which is later removed by washing with hot water. R. K. F.

Sulphur-containing Phthalocyanine Derivatives—Direct and Vat Dyes. Basf. *BP* 713,865

Phthalocyanines containing SH groups are treated with salts of halogencarboxylic or organic halogensulphonic acids; alternatively halogen- or halogenomethyl-containing phthalocyanines are condensed with organic mercapto compounds containing COOH or SO_3H. The products and their ternary sulphonium derivatives are blue dyes which dye cellulose directly from a neutral or alkaline bath, or from the vat. Thus, the Na salts of a mixture of metal-free di- and tri-(mercaptomethyl)-phthalocyanine are heated at 90°C. for 1–2 hr. in absence of O_2, with an aq. soln. of Na chloroacetate. The product is separated by adding HCl. R. K. F.

Vat Dye Pastes of Stable Viscosity. General Aniline. *BP* 715,213

Pastes of vat dyes, e.g. of chloroindanthrone, are stabilised at a low viscosity by adding 5–75% of the wt. of vat dye of a triethanolamine triester of an unsubstituted aliphatic carboxylic acid containing ≮ 4C. Thus, all parts being by weight, dichloroindanthrone (11) is ball milled for 24 hr. with water (85), lignin sulphonic acid (2) and triethanolamine tricaprylate (2) at pH 5–6. The resulting paste after adjusting the pH to 7–8 has a low stable viscosity. R. K. F.

Caramel. Union Starch & Refining Co. *USP* 2,651,576

The colouring materials are precipitated from a caramelised carbohydrate solution, filtered off and then dissolved in water in presence of a non-toxic stabiliser, e.g. propylene glycol. This gives a caramel solution of greater colouring power than has hitherto been known.

USP 2,651,577

A dry, powdered caramel of low hygroscopicity is produced by burning sugar in an open pan to a tinctorial power of 20–50 and water content 4–6%. The molten mass is then discharged on to a chilling and breaking mechanism while still heating the open pan to keep the burnt sugar molten. The chilled mass is broken and ground to yield a product of tinctorial power about 45 and containing 4·5% of moisture. C. O. C.

Carbon Black. Columbian Carbon Co. *BP* 716,849

Heavy, normally liquid hydrocarbons can be satisfactorily used for making furnace black of small particle size by injecting the hydrocarbon into a chamber where separate streams of hot blast flame gases are caused to meet with considerable impact but without serious loss in kinetic energy of motion longitudinally through the chamber.

BP 717,206

By producing a non-oxidising blast flame the yield of black is substantially increased. C. O. C

Furnace Black. Columbian Carbon Co. *BP* 715,713

Method and apparatus in which a hydrocarbon is decomposed by rapidly mixing it with a stream of hot gas passing through an elongated, heat insulated reaction chamber. A uniform product of small particle size is obtained. C. O. C.

New Method for the Purification of Direct Dyes (VIII p. 590).

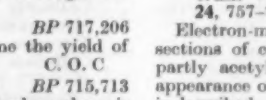
Optical Evaluation of Pigments. I— Discussion and Methods. II— Whites, Yellows, and Bright Reds (XIV p. 597).

V— PAINTS; ENAMELS; INKS

PATENTS

Dispersing Pigments in Mineral Oil Printing Inks. American Cyanamid Co. *BP* 716,458

Sulphosuccinates of formula $R^1OOC\cdot CH_2\cdot CHSO_3Me\cdot COOR^2$ (Me = alkali or alkaline earth metal; R^1 and R^2 = Alk or the residue of incompletely esterified glycerine and together contain ≮ 18C) or thiophosphatosuccinates of formula



(R^3, R^4 and R^5 = same or different Alk and together contain ≮ 18C; n = valency of Me) when present in small quantities produce excellent dispersion of pigments in mineral oil (hydrocarbon vehicle in which the aromatic content is < 50%) with markedly improved rheological properties, e.g. plastic viscosity, yield value and thixotropy, and in many cases also with improved texture and strength. C. O. C.

Dull Finish, Abrasion-resistant Baking Enamels. Lewis Berger & Sons. *BP* 716,349

Dulled finish and extreme abrasion-resistance are secured simultaneously in baking-type enamels by incorporation of 1·4–15·0% by weight of the composition of a powdered, non-plasticised vinyl halide polymer of mol. wt. about 6000 and softening point ≮ 300°F. C. O. C.

Aqueous Coating Compositions. A. Schneider. *BP* 716,652

A composition which forms with water a suspension which may be used e.g. for producing a wall-paper-like appearance on walls, comprises a fibrous material (e.g. cellulose, asbestos or glass fibres), a filler (e.g. $BaSO_4$ or $CaCO_3$) and a water-soluble starch to act as a binder and as a dispersing agent for any desired pigment. An etherifying or esterifying agent may be added to render the starch insoluble on drying. C. O. C.

Coating Composition. C. L. Betsch and F. H. Detrick. *USP* 2,650,909

A composition suitable for application to surfaces ordinarily difficult to coat and which although not requiring heat or pressure to apply can be heated or pressed to mould the material to which it is applied without injuring it consists of an acrylic resin, a pigment, and a solvent or thinner. C. O. C.

Optical Evaluation of Pigments. I— Discussion and Methods. II— Whites, Yellows, and Bright Reds (XIV p. 597).

VI— FIBRES; YARNS; FABRICS

Literature Survey on Fibre Friction. J. H. Langston and W. T. Rainey. *Text. Research J.*, **24**, 643–653 (July 1954).

Improvement of the Lustre of Cotton. VIII— Selection within Commercial Varieties on the Basis of Fibre Properties. L. Fourt, R. M. Howorth, M. B. Rutherford, and P. Streicher. *Text. Research J.*, **24**, 685–694 (July 1954).

Concentric Cellulose Layers in Cotton Fibre Cell Wall. V. W. Tripp and R. Giuffria. *Text. Research J.*, **24**, 757–758 (Aug. 1954).

Electron-microscopical observations of ultra-thin cross-sections of cotton fibres are described. Untreated and partly acetylated cotton fibres are employed, and the appearance of structural layers concentric with the lumen is described. A. B.

Variation in the Lattice Spacing of Cellulose. H. J. Willard. *J. Polymer Sci.*, **13**, 471–476 (May 1954).

A comparative study of unit cell parameters— *a*, *c*, and *β*— of a considerable number of cellulose specimens, including samples of the four structure types I, II, III, and IV, is made. Small variations are observed between samples of different origin for I and II and are most marked for the monoclinic angle parameter *β* and in the case of I. No unit cell parameter differences are found for III, but the intensity of the (020) reflection shows large variations. W. R. M.

Phosphorus Content of Egyptian Raw Cotton. A. K. Wahbi and M. S. El-Ansary. *J. Textile Inst.*, **45**, T 624–T 629 (Aug. 1954).

The phosphorus content of Egyptian raw cotton is determined colorimetrically, and is found to average 0·113%, calculated as P_2O_5. It increases with the staple length and, in common with the older varieties, is sufficiently high to distinguish the cotton from American varieties. Although it is possible that environments and plant characteristics which produce higher P content also produce cottons of higher Methylene Blue absorption,

there appears to be no other connection. Distilled water at 100°C., 0·25N-H_2SO_4 at 100°C., and 0·25N-NaOH at 100°C., each for 30 min., and distilled water at 20°C. for 24 hr., remove 80, 91, 20, and 61% of the phosphorus respectively. J. W. B.

Hydrolysis of Cellulose. I—Fine Structure of Egyptian Cotton. A. Sharples. *J. Polymer Sci.*, **13**, 393–401 (April 1954).

Kinetics of chain degradation has been studied for the heterogeneous hydrolysis of Egyptian cotton under mild acid conditions. Results are interpreted to give estimates of accessibilities free from defects associated with former measurements. The amount of accessible material in the undegraded cotton is 10·8%, but this is reduced during hydrolysis to < 5%. Recrystallisation takes place at an early stage in the degradation, starting at a point when ca. one-eighth of the intercrystalline chain segments have been broken. W. R. M.

Hydrolysis of Cellulose. II—Acid-sensitive Linkages in Egyptian Cotton. A. Sharples. *J. Polymer Sci.*, **14**, 95–104 (July 1954).

Hydrolytic study of the kinetics of chain degradation is used to detect the presence of acid-labile linkages in cotton. Results for Egyptian cotton regenerated from benzyltrimethylammonium hydroxide in absence of O_2 show that only a very small fraction of such linkages can be present in the original cotton, and these may be produced during the alkali treatment. Cotton regenerated from cuprammonium and cupriethylenediamine solutions contains randomly distributed linkages which are approx. 10,000 times more sensitive to acids than the normal glycosidic type. They appear to be formed from a limited number of special sites in the chain molecules by oxidation in alkaline solution. The number of these linkages is estimated to be one per 660 glucose residues. W. R. M.

Swelling Factor in Cellulose Hydrolysis. E. T. Reese and W. Gilligan. *Text. Research J.*, **24**, 663–669 (July 1954).

An enzyme (a factor) is present in the cellulolytic filtrates of fungi which has the ability to act on the primary wall of cotton. When placed in 18% NaOH, enzyme-treated fibre swells much more than does untreated fibre. A. B.

X-Ray Study of the Decomposition Product of the Ethylamine–Cellulose Complex. L. Segal, L. Loeb, and J. J. Creely. *J. Polymer Sci.*, **13**, 193–206 (March 1954).

Cotton remaining after removal of ethylamine possesses a crystalline component identical with the ammonia–cellulose decomposition product termed Cellulose III. Important differences between ramie Cellulose III and cotton Cellulose III are discussed, especially the ease of reconversion to Cellulose I. Data are given showing the effects of temperature and time on degree of conversion and the effect of time of immersion in ethylamine on the structure of the decomposition product. W. R. M.

Preparation of Cotton Cellulose IV from Cotton Cellulose III. L. Loeb and L. Segal. *J. Polymer Sci.*, **14**, 121–123 (July 1954).

Experimental details are given for the conversion of cellulose III (prepared from kiered cotton cellulose by treatment with ethylamine) to cellulose IV. X-Ray diffraction patterns of celluloses I, III, and IV are given. W. R. M.

Sorption of Water by Soda-boiled Cotton at Low Humidities and some Comparisons with Viscose Rayon. J. B. Taylor. *J. Textile Inst.*, **45**, T 642–T 664 (Aug. 1954).

Sorption data for regains < 11% at 25–65°C. are obtained for soda-boiled cotton and are compared with previous results on Fibro; the low R.H.–adsorption isotherms of both can be described by either the Freundlich equation or an equation comprising a Langmuir term plus a term proportional to pressure. The ratio of low-R.H.–adsorption of rayon to that of cotton is 2:1 and agrees with the ratios of the amounts of non-crystalline matter as given by other methods. Differential heat and entropy of sorption on adsorption- and desorption-conditioned cellulose are calculated. Hysteresis measurements are made, and the results discussed in terms of fibre morphology. J. W. B.

Viscosity of Dilute Solutions of Fibre Molecules. H. Giesekus. *Kolloid-Z.*, **138**, 38–40 (Aug. 1954).

Structure of Macromolecular Substances. VII—Interaction of Regenerated Cellulose Fibres with Cuprammonium Solution. B. D. Tukhlov, S. S. Frolov, and A. B. Pakshver. *J. Appl. Chem. U.S.S.R.*, **27**, 907–914 (Aug 1954).

Regenerated cellulose yarn (various viscose and cuprammonium rayons differing in degree of orientation and other properties are used) is immersed in a stirred soln. of cuprammonium hydroxide (Cu, 0·5–2 g./litre; NH_3, 100–200 g./litre), and the course of the absorption of copper by the fibre is followed by analysis of samples of the soln. withdrawn at intervals. As in previous work on the sorption of phenol by polyamide fibres (see J.S.D.C., **70**, 31 (Jan.), 316 (July 1954)), the results are closely in accord with Crank's equation (J.S.D.C., **66**, 366 (1950)), with the aid of which values are calculated for the diffusion coefficient. The values obtained vary in the way to be expected with the compactness of the fibre structure, typical values being (in cm.²/sec.) $1·2 \times 10^{-9}$ for high-tenacity viscose rayon (higher values are obtained when the rayon is first subjected to a relaxing treatment, e.g. in 6% NaOH soln. or boiling water), $2·7 \times 10^{-9}$ for ordinary viscose rayon, and $5·5 \times 10^{-9}$ for cuprammonium staple fibre; the equilibrium uptake of copper does not vary greatly for the various rayons. The rate of absorption of copper is reduced by addition of alcohol or caustic soda to the cuprammonium soln., but the equilibrium uptake of copper is greatly increased by these additions; addition of glycerol has little effect on the rate of uptake, but greatly reduces the equilibrium value attained. It is considered that, when cellulose is immersed in cuprammonium soln., two processes occur simultaneously—combination of undissociated cuprammonium hydroxide with the fibre through hydrogen bonds, and combination of hydroxyl ions, which then hold cuprammonium ions in the fibre by salt linkages. The behaviour of additives is explained in terms of their effects on these processes and of the action of the additive (e.g. glycerol) in competing with cellulose; thus, addition of caustic soda reduces the dissociation of the cuprammonium base, and sodium, rather than cuprammonium, ions tend to move in with the hydroxyl ions—the immediate rate of copper absorption is therefore less, although the ultimate uptake is much greater. As in previous work, diffusion coefficients are deduced also from the kinetics of the dimensional change of the fibre in the soln., but, as in the case of polyamide fibres, it is found, contrary to the authors' earlier views, that changes in fibre length cannot be treated as a process that proceeds precisely parallel to the diffusion process. A. E. S.

Degree of Polymerisation and its Distribution in Cellulose Rayons. I—Nitration of Rayon with Minimum Degradation; II—Relation between Nitrogen Content and Intrinsic Viscosity of Cellulose Nitrate. W. G. Harland. *J. Textile Inst.*, **45**, T 678–T 691; T 692–T 695 (Sept. 1954).

I—Regenerated cellulose can almost certainly be converted to cellulose trinitrate of nearly the same degree of polymerisation (measured by determining the intrinsic viscosity after renitrating to the trinitrate) by nitrating with a freshly prepared 75 : 20 : 5 mixture of nitric acid, acetic acid, and acetic anhydride. The fibre must be finely divided to be readily dispersed in the mixture, and should be washed by vigorous stirring with ice-cold water. Even so, what little degradation occurs takes place during the washing. Improved stability of the nitrated material is obtained by dissolving in acetone and precipitating with light petroleum; however, when stored dry under ordinary atmospheric conditions, there is still some decrease in intrinsic viscosity. A satisfactorily small degradation can be obtained also with a phosphoric acid–P_2O_5–HNO_3 mixture.

II—Industrial cellulose nitrate containing 12·22% N is further nitrated to different extents with mixtures of nitric and butyric acids, together with, in some instances, butyric anhydride. The intrinsic viscosities of the nitrated celluloses, before and after treatment with a non-degrading 75 : 20 : 5 mixture of nitric acid, acetic acid, and acetic anhydride to convert them to the trinitrates, are

determined. It is found that, as the N content increases from about 12% to about 14%, there is a rise in intrinsic viscosity from 2·7 to 3·8 dl/g. J. W. B.

Influence of Swelling Anisotropy on the Dyeing Properties of Viscose Rayon Filaments. J. Pinte and P. Rochas. *Bull. Inst. Text. France*, (46), 7–19 (May 1954).

Swelling anisotropy is mathematically defined as a ratio by means of data obtained from estimations of radial and longitudinal swelling as a function of water content. It is considered that swelling anisotropy is a measure of the degree of orientation of the cellulose chains. Treatment of rayon with formaldehyde decreases the swelling capacity in water, probably owing to the formation of methylene linkages between cellulose chains, but the swelling anisotropy is not appreciably affected, since the extent of orientation of the macromolecules remains substantially unchanged. Samples of rayon yarns varying in spinning stretch were examined. Increased spinning stretch results in increased swelling anisotropy and alters the kinetics of the dyeing process. For a direct dye of large molecular volume, increased spinning stretch of the rayon filaments causes a decrease in both the rate of dyeing and the amount of dye taken up at equilibrium, but for a direct dye of smaller molecular size the amount taken up at equilibrium remains almost constant. G. L.

Swelling of Hair and a Viscose Rayon Monofil in Aqueous Solutions. W. S. Barnard and H. J. White. *Text. Research J.*, **24**, 695–704 (Aug. 1954).

A microscopical method for measuring the swelling of nearly round single fibres is described. Measurements have been made on the swelling of human hair and viscose rayon monofil in various alkali-metal halide solutions and of the hair in HCl soln. In LiCl and LiBr soln. considerably more swelling is obtained than in water alone. A. B.

Weathering of Cellulose Acetate. J. B. Reid. *J. Textile Inst.*, **45**, T 665–T 677 (Sept. 1954).

Uneven exposure of loom-state cellulose acetate fabrics to condensation of moisture or to light causes weathering, which produces a lustre defect on delustring. Most serious is the condensation, which may either accelerate or retard the delustring, according to whether it is of short or long duration; if the material is desized before condensation, a retarding effect is always found. Retardation is due to a change, not elucidated, in the fibre itself. Acceleration appears to be caused by sorption of anionic surface-active agent present in the lubricant, the agent being adsorbed only where an aqueous solution has been formed by the localised condensation. Both effects can be eliminated by prolonged soaking in water before delustring, and methods of preventing the fault in mills are suggested. J. W. B.

Action of Light on Jute. W. G. Macmillan and H. P. Bhattacherjee. *J. Textile Inst.*, **45**, T 700–T 702 (Sept. 1954).

Jute, cotton in the vicinity of jute, cotton impregnated with 11% lignin, and cotton are exposed to light in a humidified Fade-Ometer. After 100 hr. strength tests are made and show that the presence or proximity of lignin causes degradation, probably owing to liberation of a volatile oxidising agent, possibly H_2O_2. J. W. B.

Action of Alkalis on Jute. W. G. Macmillan, A. B. Sen Gupta, and S. K. Majumdar. *J. Textile Inst.*, **45**, T 703–T 715 (Sept. 1954).

Jute is treated with different solutions of varying alkalinity, particular attention being given to the reaction with NaOH, and the loss in weight, shrinkage, and strength (dry and wet) of fibres and yarns, and the effects on twist and yarn diameter are studied. Extraction with NaOH rapidly eliminates most of the soluble constituents; a small proportion of lignin is solubilised after mild treatment, and cold NaOH does not affect the hexosan fraction. A portion of xylan and polyuronide appears to be intimately associated with the fibre, which is considerably weakened by attempted removal. Shrinkage in conc. NaOH is enhanced with increasing concentration and decreasing temperature. The swelling is accompanied by crimping, which is removed by prolonged application of tension. Wet strength of yarn falls considerably on treating with mild alkali, the dry strength decreasing slightly as the hemicelluloses are progressively removed. A fall of nearly 50%, however, occurs with cold conc. alkali, compared with a loss of only 25% in the single fibres and only a small reduction in the quality ratio of yarn spun from treated fibres. It is suggested that during the testing of treated yarn there is non-uniform distribution of applied load owing to derangement of the fibres in the yarn; in yarn spun from treated fibres there are a greater number of finer fibres effective in sharing the stress in a unit cross-section. J. W. B.

Nature of the Hemicelluloses of Jute Fibre— II. P. C. Das Gupta and P. B. Sarkar. *Text. Research J.*, **24**, 705–711 (Aug. 1954).

Hemicellulose I from jute fibre has been subjected to periodate oxidation, and from the amount of formic acid liberated under optimum conditions and from its non-reducing character, it is suggested that hemicellulose I has a branched structure. Its molecular weight has been found by the osmotic-pressure method to be about 20,000. A provisional structure is suggested for hemicellulose I. A. B.

Observations on the Histological Structure of Hemp. J. Szymanek. *Bull. Inst. Text. France*, (47), 49–57 (June 1954).

A microscopical study of hemp fibres varying in origin and botanical structure. G. L.

Histology and Chemistry of Keratin Formation. H. A. Bern. *Nature*, **174**, 509–511 (11 Sept. 1954).

Histology of Keratin Fibres. B. Manogue, M. S. Moss, and R. L. Elliott. J.S.D.C., **70**, 502–505 (Nov. 1954).

Sections of several different wool and hair fibres have been given chemical treatments alleged to isolate the "subcuticle membrane". The residues consist of parts of the cuticle, cortex, and medulla. The cortex residue is made up of cortical cell nuclei, fibrils, and thin membranes located at the boundaries of the cortical cells. These membranes are more resistant to treatment with sodium hydroxide solution and sodium sulphide solution than the major part of the cells, but are dissolved by proteolytic enzymes. The membranes are probably the material hitherto termed "intercellular cement". AUTHORS

Distribution of Cystine in the Cortex of Wool. E. H. Mercer, R. L. Golden, and E. B. Jeffries. *Text. Research J.*, **24**, 615–618 (July 1954).

The paracortex (more stable fraction) of the wool fibre, as isolated by enzymatic digestion of partly supercontracted fibres, contains considerably more cystine than the orthocortex (less stable fraction). Experiments indicate that the more reactive fraction of the cystine occurs predominantly on the orthocortical side of the fibre. A. B.

Thermal and Elastic Properties of α-Keratin. H. P. Bull. *J. Physical Chem.*, **58**, 101–103 (Feb. 1954).

The elastic coefficient of hair fibres indicates the existence of structural changes occurring at about 5% and 25% extension. The volume of the hair fibre exhibits a minimum at about 5% and a maximum at about 30% stretch. There are conspicuous and sharp maxima in the energies of activation for the decay of the stress of a hair fibre at about 5% and at about 20% stretch. Typical protein denaturants have no large effects on the elastic properties of hair, which indicates that hydrogen bonds are not primarily responsible for such properties. Emphasis is placed on the disulphide bonds. It is suggested that whatever molecular folding of the peptide chains may have been originally present in the hair follicle has been extensively deformed by the formation of interchain disulphide bonds. W. R. M.

Stress Relaxation of Fibrous Materials. III— Stress Relaxation of Wool Keratin in Water and in Salt Solutions. E. T. Kubu, F. Frei, and D. J. Montgomery. *Text. Research J.*, **24**, 659–662 (July 1954).

Dilute solutions of univalent and tervalent salts produce stress relaxation in wool keratin, the amount of relaxation varying greatly from fibre to fibre, but not depending strongly on ionic size or charge. Because the effects of dilute HCl and of cysteine on stress relaxation are not altered by previous treatment with salt solutions, it appears that the salt-sensitive linkages are neither the acid-sensitive bonds nor the cystine bonds. The salt-sensitive linkages are tentatively ascribed to highly ordered regions of hydrogen bonding. A. B.

Effect of Water Vapour on Wool. M. van Overbeke, G. Mazingue, and P. Desprets. *Bull. Inst. Text. France*, (46), 21–28 (May 1954).

An industrial process for setting the twist in yarns spun from wool consists in exposure of bobbins to water vapour. The action of water vapour can be attributed to hydrolysis of cystine bonds in the strained fibres and simultaneous formation of more stable linkages, resulting in decreased solubility in phenol of the processed material. The modification of the wool during twist-setting should not be greater than is necessary to obtain sufficient mechanical stability. The solubility of the wool in phenol is used as a measure of the chemical changes which have occurred. Temp. and time of processing must be standardised in order to obtain consistent results. It is claimed that treatment with water vapour at 70°c. for 25 min. avoids yellowing of the wool, but the affinity for acid dyes may increase. G. L.

Membrane Potentials for Keratin. M. L. Wright. *J. Physical Chem.*, **58**, 50–53 (Jan. 1954).

It is emphasised that membrane potential measurements are merely ionic transport number determinations for diffusion in the polymer. The use of the Meyer–Teorell theory for analysing membrane potential measurements to obtain the ionic mobility ratio is criticised on the grounds that it does not take into account the internal diffusion potential arising from a difference in ionic concentration gradients inside the membrane. Calculations of the boundary and internal diffusion potential components have been made using sorption data, which agree with experiment and show that the second potential can account for a large proportion of the total potential. It is suggested that, to characterise a membrane, sorption data are required. The ratio of the ionic mobilities can then be calculated, and from this the individual mobilities can be obtained, using membrane conductivity data. W. R. M.

Ionic Absorption on Wool Keratin. B. Olofsson. *J. Polymer Sci.*, **12**, 301–308 (Jan. 1954).

At low pH wool behaves as an anion exchanger. The equilibrium constant for absorption of Cl^- and SO_4^{2-} in mixtures is determined and used for a statistical check of theoretical constants. The Donnan theory is found to be inapplicable because of a non-vanishing difference in thermodynamic potential between liquid and fibre phases. Application of the Gilbert–Rideal theory shows that the energy of Cl^- and SO_4^{2-} absorption is comparable with the energy of water absorption on fibres. Conditions for the general application of the Donnan theory are discussed. W. R. M.

Interaction of Ions with Keratin. M. L. Wright. *Trans Faraday Soc.*, **50**, 89–96 (Jan. 1954).

Measurements have been made of radioactive ^{24}Na and ^{82}Br self-diffusion, membrane conductance, membrane potential, and equilibrium sorption for the horn keratin–NaBr system. Na^+ and Br^- ions are not sorbed equally, the disparity being greatest in dilute solutions. Hydrogen ions maintain electroneutrality, and can be obtained from the solution since it can absorb atmospheric CO_2. It is suggested that, when keratin and similar polymers are placed in dilute salt solutions, the net result is mainly sorption of the acid of that salt. Sorption results are discussed in terms of the Gilbert–Rideal and Donnan theories. Calculated ionic mobilities are about 0·1% of those in aqueous solution, which suggests that diffusion does not occur in liquid water contained in pores of the keratin. From diffusion and sorption results values are predicted for conductance and membrane potentials which are in agreement with experiment. The transport number, from which membrane potential, etc. can be calculated, is related to ionic concentrations and mobilities in the membrane phase. For the system considered it is shown that any variation in transport number is largely the result of the change in the ratio $[Br^-]/[Na^+]$. W. R. M.

The Combination of Wool with Acids. L. Peters. J.S.D.C., **70**, 436–441 (Oct. 1954).

Conclusions drawn by Olofsson from experiments on the combination of keratin with mixtures of sulphuric and hydrochloric acids are criticised. Inconsistencies in the data are corrected, and the results recalculated on this basis. It is shown that the statistical test employed cannot be used to decide between rival theories, and the exact meaning to be attached to t-values is illustrated by an example. A critical examination is made of the assumptions which have to be made to test the Donnan and Gilbert–Rideal theories, and the claim that these data favour the latter is rejected. AUTHOR

Combination of Wool Keratin with Alkali. J. L. Horner. *Trans. Faraday Soc.*, **50**, 1000–1010 (Sept. 1954).

The alkali titration curves of wool protein with NaOH or KOH, compared under identical conditions, are found to be the same. The effect of KOH at various cation concentrations has been studied, giving a series of titration curves which are investigated theoretically. Donnan membrane equilibrium theory has been applied to the combination of protein and alkali, and a theoretical titration curve calculated. This shows excellent agreement with experiment, and it is concluded that tyrosine reacts completely during titration and that there is a small excess of free carboxyl groups present. "Internal" pH values are calculated for various cation concentrations and lie nearly all on one curve. Application of the Gilbert–Rideal theory is difficult because of diverse affinities of basic sites, and the best theoretical curve obtained shows poor agreement with experiment. An alternative theory, based on the intrinsic behaviour of the protein, gives good agreement over only a section of the curve. W. R. M.

Basic Amino Acids of Silk Fibroin. M. C. Corfield, F. O. Howitt, and A. Robson. *Nature*, **174**, 603–604 (25 Sept. 1954).

Samples of carefully purified fibroin, from degummed silk, have been hydrolysed, and aliquots fractionated on a Dowex 50 ion-exchange column by the method of Moore and Stein (*J. Biol. Chem.*, **192**, 665 (1951)). Determinations based upon the histidine, lysine, and arginine peaks so obtained yield values corresponding closely with an integral mol. ratio of 2:3:5, and indicate that the mol. wt. of fibroin is of the order of 84,000, and that there are rather more than 1000 amino acid residues per mol. (for an equivalent residue wt. of 78). These results agree well with the value obtained by Holmes and Smith (*Nature*, **169**, 193 (1952)). J. W. D.

New Solvent for Silk. C. Earland and D. J. Raven. *Nature*, **174**, 461 (4 Sept. 1954).

Silk dissolves readily in formic acid containing small quantities of water and certain inorganic salts at room temperature, semi-solid solutions containing 20% (wt./vol.) of silk being prepared. Effective salts include LiCl, LiBr, LiI, and LiCNS; $MgCl_2$, $CaCl_2$, $SrCl_2$, $ZnCl_2$, and $MnCl_2$; and $CaBr_2$ and $BaBr_2$. The concentration of salt required is related to the water content of the acid: i.e. with 90% (by wt.) acid, 10% (wt./vol.) $CaCl_2$; with 98% acid, only 2% $CaCl_2$. Viscosity determinations indicate that there is far less degradation than in phosphoric acid. Dilution with water followed by agitation gives a white curd, the infrared absorption suggesting that this is the β-form. Films cast by evaporation show a carbonyl absorption peak characteristic of the α-configuration. J. W. B.

Chemical and Physical Aspects of Synthetic Fibres. R. Hill. *Chem. and Ind.*, 1083–1089 (4 Sept. 1954).

A review of the chemical and physical structural requirements in a polymer which lead to fibre formation, and the relationship between these factors and the properties of the fibres formed. Amongst the synthetic fibres specifically referred to and discussed are nylon, Terylene, Orlon, dynel, Saran, Acrilan, Vinyon, and polytetrafluoroethylene. J. W. D.

Development and Applications of Synthetic Textile Fibres. A. Parisot. *Bull. Inst. Text. France*, (47), 7–47 (June 1954).

A survey of the historical development, classification, and properties of synthetic fibres and fibre mixtures and a critical comparison with natural fibres. The suitability of fabrics made from various fibres for specific technological applications is discussed. G. L.

Thermal Degradation of 66-Nylon. I. Goodman. *J. Polymer Sci.*, **13**, 175–178 (Feb. 1954).

When N-substituted adipamides are heated under anhydrous conditions, CO_2 is formed without the production of equivalent amounts of hydrocarbons. The occurrence

of this reaction when 66-nylon is heated will explain the disproportionate amounts of CO_2 formed and avoids the necessity of assuming that CO_2 arises together with NH_3 by decomposition at salt links or that some CO_2 arises from sorption or from parts of the chain other than the ends. Ultraviolet absorption studies of pyrolysis residues of dialkylamides suggest that they are composed largely of substituted indoles. A similar process may occur on heating 66-nylon. W. R. M.

Electrical Potential of Nylon Fibres in Aqueous Media. F. T. Wall and P. M. Saxton. *J. Physical Chem.*, **58**, 83–86 (Jan. 1954).

The electrical potential of a nylon fibre interacting with solutions of bases is calculated from theoretical considerations and experimental data. Fibre potential is relatively insensitive to temperature changes. The number of end-groups on the fibre which must be charged to produce the potential is shown to be negligibly small compared with the number of end-groups interacting with the basic solutions. This verifies the assumption that equivalent numbers of cations and anions are absorbed by the fibre. W. R. M.

Absorption of Bivalent Bases on Nylon Fibres. F. T. Wall and P. M. Saxton. *J. Physical Chem.*, **58**, 86–90 (Jan. 1954).

Absorption of $Sr(OH)_2$ on nylon fibres has been investigated over the range 0–45 $\times$ 10^{-6} mole of base per gram of fibre. Results suggest that the bivalent cations are absorbed by the carboxyl ions in predominantly two forms— $COOSr^+$ and $COOSrOH$. Because several different reactions can occur more or less simultaneously, graphical analysis of results is difficult. Equilibrium constants for the reactions of $Sr(OH)_2$ with the fibre are calculated. The constancy of the results obtained for the range of reliable experimental data provides evidence in support of the theoretical analysis. W. R. M.

Wettability of Nylon, Polyethylene Terephthalate, and Polystyrene. A. H. Ellison and W. A. Zisman. *J. Physical Chem.*, **58**, 503–506 (June 1954).

Wettability of smooth surfaces of nylon, polyethylene terephthalate, and polystyrene has been studied by observation of the equilibrium contact angle formed by a liquid drop on the surface. A variety of liquids have been used. Comparisons show that wettability by polar hydrogen-bonding liquids is increased by the presence of both amide and ester groups in the solid surface, but to a much greater extent by the amide group. Wettability by organic liquids containing Cl, Br, or I is less affected by the amide or ester groups. Reasons are given for believing that hydrogen bonding takes place in the wetting of nylon by water, glycerol, formamide, and thioglycol, and does not take place in the wetting of polyethylene terephthalate by these liquids. W. R. M.

Pile Irradiation of Polyethylene Terephthalate (Terylene). A. Todd. *Nature*, **174**, 613 (25 Sept. 1954).

The effect upon polyethylene terephthalate of radiation, at least up to 800 MW.-hr., appears to be degradative, though possibly accompanied by branching. The relative ease of soln. (unchanged by irradiation) of all the samples in *o*-chlorophenol, together with the lowering of the softening point, is inconsistent with the presence of any measure of cross-linking as reported by Charlesby (*Ibid.*, **171**, 167 (1953)). J. W. D.

Effect of Solutions of Surface-active Agents on the Strength of Glass Fibres. M. S. Aslanova. *Doklady Akad. Nauk S.S.S.R.*, **95**, 1215–1218 (21 April 1954).

An examination is made of the tensile properties of glass fibres (aluminoborosilicate and soda–lime–silica; diameter 2–63μ.) immersed in various liquids (water, kerosene, or aq. soln. of K oleate (0·9%), Aerosol OT (Na salt of dioctyl sulphosuccinate) (0·5%), *iso*pentyl alcohol (2·5%), or Velan (0·5%)). For fibres of diameter 5·8μ. the tensile strength under rapid extension is reduced by ~20% by replacement of kerosene ($\equiv$ dry air) with water, and by up to 40% by replacement of kerosene with a soln. of surface-active agent; but the effect is reversible, since fibres dried after treatment with these liquids are of normal strength. The loss in strength increases greatly as the fibre diameter increases; it is small for fibres of diameter $< 3\mu$. If the fibres are held under tension in the liquids for a considerable time, a fatigue effect is shown and the breaking strength is greatly reduced. Thus, if fibres of diameter 5·8μ are immersed in a soln. of *iso*pentyl alcohol or Velan and placed under a tension equal to 50% of the load required for rupture in water under rapid-extension conditions, 60% of the fibres break during the first hour; if unbroken fibres are allowed to relax and are transferred to a non-polar liquid or air, their original tensile properties are recovered. The results are explained as due to adsorption of water and surface-active substances on the surface of micro-crevasses formed in the fibre during deformation, the fatigue effects being associated with the slow extension of this process to the inside of the fibre; the surface energy of the glass is lowered, and the formation and development of micro-crevasses are facilitated. The probability of the occurrence of dangerous defects on or in a fibre is greatly reduced as the fibre diameter is reduced. A. E. S.

PATENTS

Lubricating Viscose Rayon Threads. Courtaulds. *BP* 715,374

Using a cation-active or non-ionogenic agent as emulsifying agent for the lubricating oil prevents formation of deposits during lubrication and drying of the regenerated thread. W. G. C.

Modifying the Dyeing Properties of Cellulose and Cellulose Esters or Ethers. Bradford Dyers' Association. *BP* 716,233

Treatment with an aqueous solution or dispersion of the reaction products of alkali metal bisulphites with mono- or poly-functional organic *iso*cyanates or *iso*thiocyanates, and then drying and baking, preferably at the decomposition temperature of the impregnating agent, results in modification of the dyeing properties of cellulose and cellulose esters or ethers. Thus cellulose so treated has high affinity for acid, chrome, basic and disperse dyes, and increased affinity for direct dyes; cellulose esters so treated have affinity for acid, chrome and direct dyes and increased affinity for basic dyes. The treated materials have reduced swelling in water. C. O. C.

Improving the Resistance of Polyvinyl Alcohol Fibres to Water and Heat. Kurashiki Rayon Kabushiki Kaisha. *BP* 716,104

Heating dry polyvinyl alcohol fibres in the vapours of methanol and/or ethanol and/or superheated steam, if desired in presence of air, at 120–225°c. for 3–60 min., preferably at more than atmospheric pressure, followed by heating with a solution of an aldehyde in presence of an acid catalyst so as to effect partial acetalisation, improves the resistance of the fibres to water and heat. C. O. C.

Rendering Commercially Purified Acrylonitrile Colour-stable. American Cyanamid Co. *BP* 717,041

Commercially purified acrylonitrile is rendered colour-stable by adding to it 0·3–3·0% by wt. of water. C. O. C.

Acrylonitrile Copolymers. Chemstrand Corpn. *USP* 2,650,151

Copolymers of acrylonitrile with 2–20% of allyl-, methallyl- or β-chloroallylglycidyl ether are useful for forming into fibres. Treating them with ammonia, amines, or a mercaptobenzthiazole confers on them affinity for acid dyes, maximum affinity being obtained when the amino compound is converted into a quaternary ammonium salt. Alternatively the copolymer may be given the amine treatment and then dyed in presence of thiourea or an alkyl substituted thiourea. C. O. C.

Action of Carrotting Agents (XII p. 595).
Anhydrous Trifluoroacetic Acid as a Solvent for Proteins (XII p. 595).
Kinetic and Thermal Study of the Polymerisation of 7-Heptanolactam (XIII p. 595).
Macromolecular Compounds. LXI— Decarboxylation of Dicarboxylic Acids during Polycondensation (XIII p. 595).
Polymerisation of Acrylics. I— Chemistry of Polymerisation of the Acrylics. II— Acrylonitrile Copolymers and Relationship to Dyeability (XIII p. 596).
Application of Rhodamine B to Interaction Studies in Proteins and Simple Model Systems (XIV p. 600).

VII— DESIZING; SCOURING; CARBONISING; BLEACHING

Interpretation of the Conductivity of Soap Solutions. D. Stigter. *Rec. Trav. chim.*, **73**, 611–625 (Aug. 1954).

The relation between specific conductivity and concentration for micellar solutions changes sharply near the critical micellar concentration. The change is more clearly demonstrated if differentials are plotted, leading to a stepped graph. The departure of the shape of the graph from the ideal case is a sensitive test for the size distribution of the micelles. In a number of cases the micelles are found to be practically uniform in size. From data in the region of the critical micellar concentration the molecular weight of the micelle may be calculated. Anomalous conductivity curves may be explained in terms of a wide range of size distribution of the micelles. A. J.

Critical Micelle Concentration of Soap Mixtures. K. Shinoda. *J. Physical Chem.*, **58**, 541–544 (July 1954).

The critical micelle concentration (C.M.C.) of soap mixtures has been determined for the combination of seven potassium soaps— C_nH_{2n+1}·COOK (n = 5–7, 9–11, 13). A theoretical expression for the C.M.C. is derived. Experimental results are in good agreement with theory. W. R. M.

Thermodynamics of Micellar Solutions. D. Stigter *Rec. Trav. chim.*, **73**, 593–610 (Aug. 1954).

An equation is derived for the association equilibrium between single ions and micelles in soln. of association colloids. Activity corrections are deduced for the case of spherical micelles surrounded by a diffuse electrical double layer. A. J.

Relation between Viscosity and Critical Micelle Concentration of Detergent Solutions. II— Viscosity and Diffusion Coefficient of Non-ionic Detergent Solutions. H. Okuyama and K. Tyuzyo. *Bull. Chem. Soc. Japan*, **27**, 259–263 (July 1954).

From an examination of the properties of aqueous solutions of a range of polyoxyethylene non-ionic detergents, it is shown that, as for anionic detergents, η_{sp}/C (η_{sp} = specific viscosity, C = concn.) reaches a minimum at the critical micelle concentration, where there is also a sudden change in the diffusion coefficient. After the completion of micelle formation, the diffusion coefficient is constant and independent of concentration. It is concluded from the influence of electrolyte on diffusion coefficient, that salting out is due to an increase in micellar volume. Assuming a spherical micelle, the micellar mol. wt. has been calculated for the various detergents tested, with results ranging from 31,000 to 289,000. W. K. R.

Co-operation of Laundries with the Textile Industry. O. Viertel. *Textil-Praxis*, **9**, 858–863 (Sept. 1954).

Examples of complaints from practice are given, and informative garment labelling is suggested. S. R. C.

Kinetics of Bleaching with Chlorine-containing Agent. F. Gasser and R. Müller. *Melliand Textilber.*, **35**, 1001–1005 (Sept. 1954).

A study of the concentration–time graphs of the bleaching baths and consideration of the reaction rates showed that sodium chlorite does not damage native cotton (I) or regenerated cellulose (II), whilst *p*-toluenesulphochlorimide (Activin) affects II only. Sodium hypochlorite acts equally on I and II. S. R. C.

Bleaching of Wool with Chlorite Solutions. C. Schirlé and J. Meybeck. *Bull. Inst. Text. France*, (45), 31–63 (April); (46), 29–68 (May 1954).

A detailed description of a bleaching process for wool with cold acidified chlorite soln. Phosphoric acid or an acetate–acetic acid buffer is used to adjust the pH. Stainless-steel equipment is suitable without risk of corrosion. It is claimed that the method is quicker than the hydrogen peroxide bleach for wool, and that the process may be combined with hypochlorite shrink-resisting treatment. G. L.

Non-ionic Detergents (III p. 578).

VIII— DYEING

Vertical and Horizontal Organisation (with particular reference to the Finishing Section of the Textile Industry). W. Crossley. *J. Textile Inst.*, **45**, P 504 P 529 (Aug. 1954); *Colour and Textiles (Proc. Joint Conference)*, pp. 164–189.

Dyeing of Textile Fibres under Pressure. L. Drijvers. *Melliand Textilber.*, **35**, 1014–1018 (Sept. 1954).

The dyeing of wool, cellulosic, and man-made fibres by the Steverlynck static process (which employs a constant gas pressure, controlled by a centrifugal pump, above the liquor) at temperatures exceeding 100°C. is described. This system is claimed to stabilise other bleaching and dyeing operations and to reduce the amount of hydrosulphite necessary in vat dyebaths. S. R. C.

Substantivity of Dyes. H. Wahl. *Teintex*, **19**, 667–683 (Sept. 1954).

A critique of post-war physicochemical investigations carried out by various workers. 34 References. S. R. C.

New Method for the Purification of Direct Dyes. B. N. Mel'nikov and P. V. Morŷganov. *J. Appl. Chem. U.S.S.R.*, **27**, 915–920 (Aug. 1954).

Direct dyes may be purified by treatment with Aniline Black, which acts as a basic ion-exchange material. The Aniline Black is freshly prepared by boiling a mixture of the following three solutions— aniline hydrochloride (25 g.) in water (80 ml.) at 75°C., copper sulphate (5 g.) and sodium chlorate (9 g.) in water (50 ml.) at 75–80°C., and ammonium chloride (4 g.) in water (50 ml.) at 75°C.; it is filtered off, washed, and added in the form of a paste to a boiling soln. of 5–7 g. of impure or commercial direct dye in 500 ml. of water. When all the dye has been absorbed by the Aniline Black, the mixture is filtered, and the residue is extracted with boiling water until a negative chloride test is obtained in the extract. The residue is then treated with the theoretical amount of caustic soda, when the dye passes into soln. The soln. is concentrated by evaporation, and the dye is precipitated with ethanol. In one such treatment a 46·2% preparation of Direct Sky Blue FF yielded a product of 94·3% purity. A. E. S.

Realisable Colour Gamuts in Dyeing. E. Atherton, D. A. Garrett, and T. Vickerstaff. *J. Textile Inst.*, **45**, P 350–P 368 (Aug. 1954); *Colour and Textiles (Proc. Joint Conference)*, pp. 10–28.

Patterns of fabric or yarn are dyed with basic, level-dyeing acid, azoic, milling acid, chrome, Carbolan, direct cotton, fast-to-light direct cotton, indigoid vat, pre-metallised chrome, vat, and sulphur dyes, and their tristimulus coefficients measured. The appropriate lightness plane in the Vickerstaff colour solid is selected, and the trichromatic co-ordinates of the limit of attainable colour are determined at the appropriate wavelength. From this colour gamuts are drawn and the ratios of real to theoretical gamut calculated; they fall, in the order of dyes listed above, from 0·58 for basic dyes (on silk) to 0·11 for sulphur dyes (on cotton), and thus bear out the generally accepted trade opinion on the performance of these classes of dyes. Results, and scope for improvement, are briefly discussed. J. W. B.

Use of Coloured Fibres in Yarns. H. Beevers. *J. Textile Inst.*, **45**, P 462–P 479 (Aug. 1954); *Colour and Textiles (Proc. Joint Conference)*, pp. 122–139.

The use of coloured fibres in the wool industry, methods of mixing (including mélange printing), speciality coloured worsted yarns, and the effects of various factors on the appearance of coloured yarns are discussed. J. W. B.

The Designer's Approach to Colour. A. Morton. *J. Textile Inst.*, **45**, P 497–P 503 (Aug. 1954); *Colour and Textiles (Proc. Joint Conference)*, pp. 157–163.

Influence of the Substrate upon the Light Fading of Azo Dyes. H. R. Chipalkatti, N. F. Desai, C. H. Giles, and N. Macaulay. J.S.D.C., **70**, 487–501 (Nov. 1954).

Several series of simple phenylazonaphthalene dyes, both water-soluble and water-insoluble, have been applied to a

variety of substrates, and the relative fading rates of the dyes in each series on each substrate have been compared with the Hammett σ-values of *meta* and *para* substituents in the benzene nucleus. The conclusions reached may be summarised thus—

(*a*) All the substrates used fall distinctly into two classes, according to the sense in which they influence the relative fading rates, viz. (i) proteins, i.e. wool, silk, and gelatin; and (ii) all other materials, including cellulose, cellulose esters and ethers, and nylon.

(*b*) The protein substrates may perhaps take part chemically in the fading reaction, most probably by reduction of the dye. The reaction does not appear to involve either the peptide linkages or the hydrocarbon portions of the protein molecules, but may perhaps involve the tyrosine or histidine side-chains.

(*c*) The non-protein substrates perhaps do not take part, chemically, in the fading reaction, which is considered to be oxidative in the absence of protein.

AUTHORS

Mohair Pile Sealskin Fabric. Anon. *Dyer*, **112**, 353–355 (3 Sept.); 431–432 (17 Sept. 1954).

High-class sealskin pile fabric contains a cotton backing dyed with sulphur dyes, the warps on beams and the weft in hanks or on cheeses using dyes fast to acid cross-dyeing. The mohair pile is cross-dyed with acid or chrome dyes. Finishing is an important operation and consists in pressure steaming for 30–60 min. at 5–10 lb./sq. in. pressure, the material being suspended on rails fitted with tenter hooks, steamed in a cylindrical steam box, and covered with a woollen blanket to avoid contact with flying spray. The process is repeated after the position of the cloth has been altered to ensure even treatment. After steaming, the cloth is "lacquered" to improve its lustre. Lacquering consists in mechanically applying a paste of egg albumen and wheaten flour by means of rotating brushes, drying, steaming for 30–60 min. at 5–10 lb./sq. in., washing off, and dyeing. Unlevel lacquering can result in uneven dyeing. After dyeing, the cloth is relacquered, carded, tentered, and sheared. In some cases the cloth has a "cladded" cotton foundation or backing material. Rubber may also be applied to the cotton cladding. The application of British gum or cellulose ester products to the backing gives an imitation natural-hide effect. Natural skin markings are imitated by printing with direct cotton dyes with the addition of ammonium oxalate to the printing paste to assist fixation. Aniline Black and permanganate are also used.

B. K.

Measurements of Redox Potential in Continuous Vat Dyeing. K. Neufang. *Melliand Textilber.*, **35**, 1012–1014 (Sept. 1954).

By measurement of the p.d. of Pt–calomel electrode systems operating in contact with moving fabric in the inside and at the exit of a steamer, control of the hydrosulphite content is possible. It is shown that colour yield and levelness are connected with the relative potential values inside and outside the steamer: the smaller the difference the better the results obtained.

S. R. C.

Some Factors in the Measurement of Affinities of Vat Dyes for Cellulose. R. H. Peters and J. Simons. J.S.D.C., **70**, 557–563 (Dec. 1954).

Isotherms have been obtained for the adsorption of Caledon Red BN and Caledon Red 5G by cuprammonium rayon yarn at 40°C., in the presence of varying concentrations of sodium chloride and sodium hydroxide. It is shown that consistent values for the affinity of these dyes are obtained only when account is taken of the absorption of hydroxyl ions by the fibre. The use of the "equivalent chloride" ion concentration in calculating the affinity is discussed and shown to be satisfactory.

AUTHORS

Investigation of Sodium Formaldehyde-sulphoxylate as the Primary Reducing Agent in Vat Dyeing. AATCC South Central Section. *Amer. Dyestuff Rep.*, **43**, P 525–P 540 (16 Aug. 1954).

At temperatures above 150°F. the reduction potentials of sulphoxylate under dyeing conditions become comparable with those of the usual alkaline hydrosulphite baths employed in the conventional manner below 150°F. Laboratory procedures are worked out to permit production-scale batch dyeings at liquor ratios of 8 : 1 and 20 : 1, and the optimum conditions for penetration, levelness, and exhaustion are determined. Numerous recipes are given, including special procedures for a wide range of synthetic fibres. The method offers easier and better control of rate of exhaustion, low strike, increased leuco stability at high temperatures, particularly with halogenated indanthrones, and increased stability of reducing agent.

J. W. B.

Dyeing Jute with Tannins of Garan. S. M. Ala-ud-Din and M. Ahmed. *Pakistan J. Sci. Research*, **5**, 121–123 (in *Pakistan J. Sci.*, **5**, (4)) (1953): *Chem. Abs.*, **48**, 11064 (25 Sept. 1954).

Tannin from garan, *Ceriops roxburghiana*, used with chrome, iron, and copper, gives dyeings on jute of reasonable fastness to light and good fastness to washing.

C. O. C.

Dyeing of Cellulose Acetate with Non-ionic Dyes. I—Absolute Heats of Association. T. G. Majury. J.S.D.C., **70**, 442–445 (Oct. 1954).

The heats of dyeing of five "model" dyes on cellulose acetate have been measured. By combining these with the heats of solution and sublimation of the dyes, the absolute heats of association between dyes and substrate may be evaluated. This has been done for the two dyes for which data on heats of sublimation are available; values of the order of — 20 kcal./mole are obtained. The bond energies appear to be chiefly ascribable to interaction between the permanent dipoles of the carbonyl groups in the substrate and permanent or induced dipoles in the dye molecules. There are indications in the two cases examined that, if intermolecular hydrogen bonds exist in the dye crystals, then hydrogen bonds may reasonably be postulated also between the dyes and the substrate.

AUTHOR

Dyeing of Cellulose Acetate with Non-ionic Dyes. II—Rates of Diffusion and their Relation to Dyeing Affinity. T. G. Majury. J.S.D.C., **70**, 445–447 (Oct. 1954).

Measurements of the rates of dyeing of five "model" dyes on cellulose secondary acetate and triacetate have been used to evaluate the apparent diffusion coefficients of the dyes. The coefficients are shown to have a twofold activation energy: one part is identifiable with the free energy of dyeing, and the other is attributable to mechanical obstruction of the diffusing dye by the body of the substrate. This suggests that a dye molecule penetrating cellulose acetate undergoes alternate absorption by the acetate and dissolution by the water, and that diffusion takes place in the aqueous phase.

AUTHOR

Dyeing of Cellulose Acetate from the Vapour Phase. T. G. Majury. J.S.D.C., **70**, 448 (Oct. 1954).

Study of the cellulose acetate–dye vapour–solid dye system may lead to a method of measuring the absolute bond strength between dye and substrate. Five model dyes dye satisfactorily from the vapour phase.

C. J. W. H.

Azoic Dyeing of Acetate Rayon. I. M. S. Walls. J.S.D.C., **70**, 429–436 (Oct. 1954).

The reasons why azoic dyes cannot be applied to acetate rayon by the technique used with cotton or viscose rayon are reviewed, and the "modified azoic" technique, in which the base and the coupling component are applied to the fibre in one bath and development is carried out *in situ* in a second bath, is described. A range of coupling components have been applied to acetate rayon from neutral and from weakly alkaline baths, the latter with and without common salt, and the uptakes have been measured. Similarly the exhaustions of diazo compounds have been determined. This information is used as a guide to the most suitable azoic components for acetate rayon, and to the conditions under which they should be applied. An investigation has been carried out into the ratio in which the coupling and diazo components should be mixed when they are applied to the fibre together, and the preferred diazotisation and coupling conditions have been determined. The factors involved in the soaping after-treatment are discussed and the recommended soaping conditions are described. The light fastness assessments of a wide range of azoic combinations on bright acetate rayon are tabulated.

AUTHOR

Spun-coloured Fibres and Yarns. E. Butterworth and A. S. Cluley. *J. Textile Inst.*, **45**, P 427–P 461 (Aug. 1954); *Colour and Textiles* (*Proc. Joint Conference*), pp. 87–121.

The production and the properties of spun-dyed fibres, with particular reference to viscose and acetate rayons, are described. Shade limitations can to some extent be met by blending, and three C.I.E. co-ordinate diagrams are presented as examples of how to calculate the required proportions without actually making a blend. Comparisons are made of the cost of spun-coloured and normally dyed fibres, and of their behaviour when exposed to light and weathering. Fastness ratings of a wide range of colours to numerous treatments are tabulated for viscose rayon, Seraceta, and extra-bright Seraceta. Ten of the fastness tests have been specially developed and are described.

J. W. B.

Colour and Design in Knitwear. J. C. H. Hurd. *J. Textile Inst.*, **45**, P 480–P 496 (Aug. 1954); *Colour and Textiles* (*Proc. Joint Conference*), pp. 140–156.

Dyeing of Yarns and Fabrics containing Mixed Fibres. R. C. Cheetham and J. S. Ward. *J. Textile Inst.*, **45**, P 380–P 394 (Aug. 1954); *Colour and Textiles* (*Proc. Joint Conference*), pp. 40–54.

Advantages and disadvantages of dyeing before or after fibre blending, the influence of customers' requirements, and the effect of processing conditions on the fibres are discussed with reference to Fibro–wool, Fibro–Fibrolane, wool–Fibrolane, and blends of the three. A number of recipes are given.

J. W. B.

Dyeing of Fabrics made from Fibro and Blends containing Fibro. R. A. McFarlane. *J. Textile Inst.*, **45**, P 395–P 414 (Aug. 1954); *Colour and Textiles* (*Proc. Joint Conference*), pp. 55–74.

The use of 100% Fibro and of blends of Fibro, Fibroceta, Fibrolane, and nylon in fabrics is discussed. Details of dyeing routines for 100% Fibro and faults arising therefrom, Fibro–Fibroceta blends, Fibro–Fibrolane blends, and Fibro–nylon blends, and of the finishing of 100% Fibro and blends of the other fibres with Fibro, are presented. The finishing section includes a description of crease-resist, softening, and shrink-resist finishes.

J. W. B.

Dyeing of Felt. I— The Effect of Factory Conditions on Quality. II— An Investigation into Wool-felt Dyeing. D. Haigh. J.S.D.C., **70**, 539–547; 547–553 (Dec. 1954).

I— Under practical dyeing conditions the quality of hat felt, as represented by tensile strength and density, is affected by time and temperature of dyeing, and degree of agitation in the dyeing machine. Types of dyeing machine are compared, and the superiority of the cone dyeing machine is established, especially at the lower temperatures.

II— The quality of wool felt, as judged by tensile strength and density, is shown to be influenced by the stage at which dyeing takes place during the felting sequence, the type of dye used, and the time of dyeing. A series of laboratory experiments, using the Furness milling stocks for felting the wool patterns, indicated that the best results are obtained by dyeing at as early a stage as possible for short times with dyes of the acid milling type. The practical limitations are discussed, and preliminary results from factory trials which confirm these findings are quoted.

AUTHOR

Nylon coloured with Large Vat Dye Particles. W. H. Sharkey and F. C. McGrew. *Text. Research J.*, **24**, 633–636 (July 1954).

The presence of relatively large particles of a vat dye in nylon has been found to give outstanding light fastness. Large particles of Ponsol Red BN were incorporated in the fibre by dispersal in the polymer before spinning, giving a Fade-Ometer fastness of over 200 hr. Experiments with other dyes confirm this observation.

A. B.

Dyeing and Finishing of Polyacrylonitrile Piece Goods. J. Müller. *Melliand Textilber.*, **35**, 1006–1012 (Sept. 1954).

The practical aspects of dyeing with Anthrasol, Celliton, Astrazon dyes (CFM) above 100°c. and with acid dyes by a modified cuprous-ion technique are described and the disadvantages considered. The use of emulsified lipophilic ester salts in the dyebath increases the affinity of Anthrasol dyes, allowing dyeing to be carried out below the boil. The setting and antistatic finishing of Pan fabrics are mentioned, and a number of proprietary waterproofs on them are compared.

S. R. C.

PATENTS

Improving the Wet Fastness of Acid Dyes on Nylon. ICI. *BP* 715,919

Aftertreatment with a sulphonated derivative of naphthalene, e.g. the disodium salt of the condensate of naphthalene-2-sulphonic acid with formaldehyde, improves the wet fastness of acid dyes on superpolyamide fibres.

C. O. C.

Hair Dyes. Société Anonyme Sarmio. *BP* 716,950

An oxidation dye is mixed just before use with a paste containing H_2O_2, the viscosity of the paste being such that after the dye is mixed with it the paste does not flow on the scalp when applied to the hair.

C. O. C.

Colouring Aluminium and its Alloys Brown or Bronze. United Anodising. *BP* 716,119

The metal is given an absorbent oxide coating and is then treated with a solution containing an iron salt, a stabiliser and a compound containing at least one benzene nucleus substituted by $\geq$ 2 hydroxyl groups, e.g. pyrogallic, gallic or rufigallic acid. There should be 1–2 atoms of iron to 3 mol. of stabiliser.

C. O. C.

Colouring and Drying of Sheets of Paper, Cloth or the like (I p. 578).
Historical Notes on the Wet-processing Industry. V— Sir William Perkin (IV p. 579).
Modifying the Dyeing Properties of Cellulose and Cellulose Esters or Ethers (VI p. 589).
Acrylonitrile Copolymers (VI p. 589).
Polymerisation of Acrylics. I— Chemistry of Polymerisation of the Acrylics. II— Acrylonitrile Copolymers and Relationship to Dyeability (XIII p. 596).
Fugitive Tinting (XIV p. 597).
Application of Rhodamine B to Interaction Studies in Proteins and Simple Model Systems (XIV p. 600).

IX— PRINTING

Resists under Indigosols. P. Diserens. *Dyer*, **112**, 515–519 (1 Oct. 1954).

A survey of the various methods by which white and coloured resists under Indigosol grounds may be obtained. Alkalis, reducing agents (or more usually mixtures of the two), quaternary ammonium salts, metallic salts, amino–formaldehyde precondensates, albuminoid substances, bentonite, and various water-repellent compounds can be used as the resist, which is printed on white cloth or on cloth previously padded with Indigosol and dried (so called discharge process). The latter may cause difficulties owing to premature oxidation of Indigosol, and for this reason the former is preferred. Development of the Indigosol by the thiocyanate process involves a supplementary steaming after padding; therefore the nitrite process is used, and in this development is carried out by immersion in H_2SO_4 followed by neutralising, washing, soaping, and drying. This method is described in detail with appropriate recipes, and an outline sketch is shown of machinery to carry out this technique.

A. H.

PATENTS

Zirconium Salts as Assistants in Printing with Vat Dyes. American Cyanamid Co. *USP* 2,650,152

Addition of a zirconium salt to a vat dye printing paste (using $\frac{1}{4}$–5 times the wt. on the dye) results in prints of increased strength even if they are stored in a humid atmosphere before ageing.

C. O. C.

Metallic Gloss Prints. Grasser & Co. *BP* 716,038

Cloth, leather or paper is printed with a paste containing metal powder, a synthetic resin precondensate, a thickener and, if desired, a catalyst and a dye or pigment. The resulting print is protected against mechanical and chemical effects by overprinting it with a second layer of synthetic resin not containing a metal powder, this layer being applied in the same pattern as the metal print. The unprinted portion may then be dyed, swollen, or otherwise treated, e.g. calendered, to increase the contrast between it and the printed areas.

C. O. C.

Pattern Effects combined with Permanent Mechanical Effects on Woven Fabrics. Heberlein & Co. *BP* 716,002

Fabric containing yarns of natural or regenerated cellulose mixed with similar yarns that have been submitted to a nitration process is printed with a synthetic resin precondensate, mechanically treated, e.g. glazed or embossed, cured and then treated with caustic alkali to destroy the nitrated yarns on the non-printed areas. The treatment with alkali has practically no influence on the mechanical effects. C. O. C.

Application of Transfers. Hermann Schott. *BP* 717,091

Prints having excellent adhesion to any material can be obtained with transfers, e.g. those based on pigmented oil varnish, by first coating the surface to be decorated with a thin layer of an aqueous dispersion of a polyacrylic or polymethacrylic ester. Alternatively the ester layer may be applied to the transfers before they are brought into use. C. O. C.

X— SIZING AND FINISHING

Permanent Finishes on Textiles. M. A. Pradon. *Teintex*, **19**, 649–665 (Sept. 1954).

Crease-resisting (I), dimensionally stable (II), mechanical (III), waterproof (IV), and fireproof (V) finishes, mostly based on proprietary products, are considered. The finishes discussed are— (I) Ureol AC (Ciba) and Lyofix DM (Ciba); (II) Sanforize (Cluett-Peabody), Rigmel (B.D.A.), Sanforset (Cluett-Peabody), acetylation of cellulose, and melamine–formaldehyde and keto resins; (III) glazing and embossing with Lyofix (Ciba) brands; (IV) Velan PF (ICI), Zelan AP (DuP), Cerol WB (S), Phobotex (Ciba), Quilon (DuP), DeCetex 104 (Dow), and Rhodorsil Waterproof 82T; (V) Erifon (DuP), Pyroset (American Cyanamid Co.), and Pyrovatex (Ciba). A description of the application of Fixer 611 conc. (Ciba) in flock finishes concludes the review. S. R. C.

Improvement of Lustre of Cotton. IX— Thermosetting Resins. L. Fourt and H. J. Elliott. *Text. Research J.*, **24**, 779–784 (Aug. 1954).

The increase of lustre resulting from the application of thermosetting resins to a cotton twill is found to be as large in range as that produced by mercerisation and to be generally similar in appearance. Further increases in lustre can be obtained by embossing. Various types of urea–formaldehyde and melamine–formaldehyde resins are very similar in their effects on lustre. A. B.

Reaction of Cotton with β-Propiolactone in the Presence of Organic Solvents. I— Purified Cotton. II— Raw Cotton. G. C. Daul, R. M. Reinhardt, and J. D. Reid. *Text. Research J.*, **24**, 738–743, 744–747 (Aug. 1954).

I— When purified cotton is treated with β-propiolactone in organic solvents, etherification occurs, apparently followed by polyesterification of the attached groups by additional lactone. Increases in the extent of reaction were obtained by "activation" of purified cotton with acetic acid before treatment with β-propiolactone.

II— It is shown that the non-cellulosic alkaline salts, naturally present in raw cotton, catalyse the reaction with β-propiolactone and make possible gains in weight of over 200%. Mercerisation, increase in twist, and the presence of natural waxes and of excess moisture adversely affect the reaction. A. B.

Chemical Reactivity of Ethylamine-treated Cotton as indicated by Acetylation. L. Loeb and L. Segal. *Text. Research J.*, **24**, 654–658 (July 1954).

The chemical reactivity of cotton "decrystallised" by treatment with anhydrous ethylamine has been compared with that of untreated and with that of mercerised cotton, the degree of acetylation achieved under comparable conditions being used as criterion. Full reactivity of the amine-treated cotton and the mercerised cotton could be maintained only if drying was avoided after treatment. The rate of acetylation and the degree of substitution obtained with an amine-treated cotton appear to increase strongly as a function of presoak time in glacial acetic acid. A. B.

Impregnation of Cloth with Resin Dispersions. H. Anders. *Textil-Praxis*, **9**, 876–878 (Sept. 1954).

The influence of time of impregnation, concentration, and pH of five types of synthetic resin dispersions is examined. S. R. C.

Crease-resisting of Cellulosic Textiles. C. van Bochove and G. J. Schuringa. *Textil-Rund.*, **9**, 451–461 (Sept. 1954).

Consideration of the mechanism of the processes using formaldehyde resins and of those using formaldehyde or glyoxal only leads to a new method employing bis-(hydroxymethylamides) of aliphatic dicarboxylic acids, $HOCH_2{\cdot}NH{\cdot}CO{\cdot}[CH_2]_n{\cdot}CO{\cdot}NH{\cdot}CH_2OH$ (cf. Gagliardi and Nuessle, *Amer. Dyestuff Rep.*, **40**, 409 (1951)). These condense to form flexible cross-links. The stiffness of the fibres is hardly affected, and hence extension at break is reduced much less than in the older methods. The cross-links aid recovery from extension and, depending on the magnitude of n, act as a plasticiser. The condensation has to be carried out at a pH of about 2·5, the tensile strength falling up to 20% in consequence, but satisfactory crease-resistance, slightly less than that obtained with resins, was achieved both on cotton and on linen. Unlike urea–formaldehyde resin, these cross-links are remarkably stable to washing and even to boiling 0·1N-NaOH. That the mechanism is due to cross-linking and not to resin formation is implied by facts such as that treated material after immersion in acetate buffer (pH 4·5, 90°C., 1 hr.) has a much lower cuprammonium fluidity than an untreated sample. 32 References. H. E. N.

Solubility of Chemically Modified Wool in Acid and Alkali. H. Zahn and A. Wurz. *Bull. Inst. Text. France*, (45), 75–83 (April 1954).

Treatment of wool with 4N-HCl at 65°C. for 1 hr. dissolves it to an extent similar to that obtained by the alkali solubility method of Harris using 0·1N-NaOH soln. Dil. H_2SO_4 soln. is not suitable, since it is difficult to remove from wool by washing and has a tendency to form sulphamic acid. Samples of wool treated with various reagents were tested for solubility by the acidic and alkaline methods. Dry chlorination of wool increases its solubility in acid by 30% and in alkali by 10%, whilst formaldehyde treatment reduces the solubility to the same extent by both methods of analysis. G. L.

Modification of Wool by the Application of Linear Synthetic Polyamides. IV— Application from Aqueous Medium. D. L. C. Jackson. *Text. Research J.*, **24**, 624–629 (July 1954).

N-Alkoxymethylpolyamides may be applied to wool from aqueous dispersions containing a surface-active agent. Using a sodium *sec.*-alkyl sulphate as anion-active detergent and a resin : detergent weight ratio of 20 : 1, ethoxymethylnylon has been applied to wool fabric from aqueous dispersions at approx. pH 2·5. The felting shrinkage can be reduced appreciably by depositing about 6% of resin in this way. A. B.

Cross-linking of Casein Bristle Fibre. R. F. Peterson, R. L. McDowell, and B. J. Harrington. *Text. Research J.*, **24**, 747–753 (Aug. 1954).

A method consisting in treating formaldehyde-hardened casein products with resorcinol and formaldehyde, drying, and heating is described for reducing the rate of uptake of water by casein fibres and plastics. The results indicate that resorcinol forms cross-links with casein and formaldehyde, resulting in an increase in wet strength. A. B.

PATENTS

Rendering Cellulosic Textiles Dimensionally Stable. Bradford Dyers' Association. *BP* 716,236

Textiles wholly or partly made of cellulose or cellulose derivatives are impregnated with the reaction product of an alkali metal bisulphite with a mono- or polyfunctional *iso*cyanate or *iso*thiocyanate before, during or after impregnation with an amide, amidine or amino triazine. The process is suitable for material of high shrinkage potential. C. O. C.

Rendering Mechanical Effects more Resistant to Water or Steam. Bradford Dyers' Association. *BP* 716,232

Mechanical finishes of improved resistance to laundering and moisture are obtained by impregnating the fabric with an aqueous solution or emulsion of the reaction products

of alkali metal bisulphites with mono- or polyfunctional organic *iso*cyanates or *iso*thiocyanates followed by drying and mechanical treatment with or without subsequent baking. C. O. C.

Retention of Fillers in Textiles. Bradford Dyers' Association. *BP* 716,234

Filled finishes on textiles are rendered resistant to washing by treating them with the reaction product of an alkali metal bisulphite with a mono- or polyfunctional organic *iso*cyanate or *iso*thiocyanate before, during or after filling, and then baking to decompose the bisulphite-cyanate compound. C. O. C.

Reducing the Felting Power of Wool. Precision Processes (Textiles). *BP* 716,203 *BP* 716,888

Very even treatment is secured when wool, if desired mixed with other fibres, is treated with aqueous *N*-bromo-acetamide at pH $\gtrsim$ 3 or aqueous *N*-bromosuccinimide at pH $\gtrsim$ 6. C. O. C.

Reducing the Shrinking Properties of Wool-Polyethylene Terephthalate Fibre Mixtures. ICI. *BP* 715,851

When Terylene is blended with wool its physical properties are not impaired when the blend is chlorinated. C. O. C.

Accurate Adjustment of the Shearing Height. Blin & Blin. *BP* 716,204

After the height of the ledger blade has been adjusted by conventional means in accordance with the thickness of the cloth in the first piece of a batch, combined measure is taken of this height and the thickness by using precision means whereby predetermined pressure is applied to the cloth. For succeeding pieces of the same batch the blade is adjusted until the readings of the measuring device indicate that it has been displaced through a distance equal to the algebraic difference between the thickness of the first piece and the thickness of the succeeding pieces measured under the same pressure. C. O. C.

Photographic Reproduction Cloth. J. Halden & Co. *BP* 716,546

Good adhesion of both the water-proofing film-forming layer and the light-sensitive emulsion is obtained by treating the base cloth with a dispersion of oils, fats and waxes and a resin and an emulsifying agent preferably one soluble in the oil and wax used. The cloth is then friction calendered and then treated successively with (*a*) an aqueous emulsion containing cellulose nitrate dissolved in a soluble solvent, a colloid and an emulsifying agent, (*b*) a non-aqueous waterproof coating, e.g. cellulose nitrate or ethyl cellulose, and (*c*) a photographic emulsion. C. O. C.

Porous Flexible Sheets of Bonded Fibres. Carl Freudenberg. *BP* 716,178

A carded lap of fibres is treated on one side with an adhesive after first passing it, if desired, between heated pressure rollers. It is then impregnated with a frothy aqueous emulsion of synthetic and/or natural rubber and/or adhesive synthetic resins. The emulsion may also contain vulcanising agents, fillers, colouring materials, etc. C. O. C.

Coated Fabric. DuP. *USP* 2,650,170

Pyroxylin coated or impregnated fabric is heated on the uncoated side with an aqueous dispersion containing polyvinylacetate, an inorganic inert filler and starch. This prevents the coated fabric curling when cut and renders any embossing applied to them much more durable. C. O. C.

Phosphorescent Coated Textiles. J. Goldstein. *USP* 2,650,169

The material is given a base coating which imparts a pure white reflecting surface. On this is superimposed firstly a coating of 2·5–6·0 oz. per sq. yd. containing phosphorescent crystals and finally a protective coating for the crystals. C. O. C.

Embossed Pile Fabric. Dunlop Rubber Co. *BP* 717,161

Pile fabric, in which the pile is fixed to the backing by a layer of a thermoplastic composition is heated to render this layer plastic after which part of the pile is pressed into it. Very sharp embossed effects may be produced. C. O. C.

Some Applications of Organic *iso*Cyanates (III p. 579).
Weathering of Cellulose Acetate (VI p. 587).
Effect of Water Vapour on Wool (VI p. 588).
Modifying the Dyeing Properties of Cellulose and Cellulose Esters or Ethers (VI p. 589).
Improving the Resistance of Polyvinyl Alcohol Fibres to Water and Heat (VI p. 589).
Vertical and Horizontal Organisation (with particular reference to the Finishing Section of the Textile Industry) (VIII p. 590).
Mohair Pile Sealskin Fabric (VIII p. 591).
Dyeing of Fabrics made from Fibro and Blends containing Fibro (VIII p. 592).
Dyeing and Finishing of Polyacrylonitrile Piece Goods (VIII p. 592).
Improving the Wet Fastness of Acid Dyes on Nylon (VIII p. 592).
Pattern Effects combined with Permanent Mechanical Effects on Woven Fabrics (IX p. 593).
Coating Paper, Films, etc. (XI this page).
Action of Carrotting Agents (XII p. 595).
Permanent Protection of Cellulosic Materials against Micro-organisms (XIV p. 599).

XI—PAPER AND OTHER CELLULOSIC PRODUCTS

Moisture Regain and Accessibility of Cellulose Derivatives. L. Valentine. *Text. Research J.*, **24**, 670–672 (July 1954).

The accessibility of various polymers has been calculated from the moisture regain and the degree of substitution. Results indicate that the method will be useful in characterising cellulose derivatives. A. B.

Viscosities of Dilute Solutions of Cellulose Acetate. W. R. Moore and J. Russell. *J. Colloid Sci.*, **9**, 338–346 (Aug. 1954).

Viscosity and precipitation results for a primary cellulose acetate are compared with those for a secondary acetate of the same chain length. Possible factors leading to variations in intrinsic viscosity with solvent and acetyl content are discussed. A tentative interpretation, based on possible configurations of the cellulose chain involving intramolecular hydrogen bonding, is advanced to account for such variations with type of solvent and acetyl content. W. R. M.

Blistering of Cellulose Acetate in Chloroform. D. M. Cates and H. J. White. *Text. Research J.*, **24**, 675–676 (July 1954).

It has been observed that immersion of cellulose acetate in chloroform causes blisters to appear on the surface, similar in appearance to those produced on wool in the Allwörden reaction. It is considered probable that the blistering reflects some form of inhomogeneity. A. B.

Hydrolysis of Cellulose Acetate Sulphate in Acetone. K. Keirstead and J. Myers. *Canadian J. Chem.*, **32**, 815–822 (Sept. 1954).

When cellulose acetate sulphate is dissolved in acetone, the hydrolysis of the sulphate ester is rapid compared with that of the acetate ester. In 70% acetone the relative rates are reversed. Hydrolysis of the sulphate ester in acetone is markedly affected by temperature. At 25°C. or above hydrolysis is complete after 24 hr. A potentiometric titration method has been developed for estimation of sulphuric acid in the presence of smaller amounts of acetic acid. W. R. M.

PATENT

Coating Paper, Films, etc. Kodak. *BP* 716,080

The paper etc. is led past a device which deposits a ribbon of flowing coating composition on to it, the two sides of the rubber extending between the coating device and the paper being subjected to different gaseous pressure, that on the side of the ribbon facing the direction from which the paper is led being less than that on the other side. This enables the presence of a splice in the paper to be disregarded without wastage and also enables a higher speed of coating than has hitherto been possible. C. O. C.

Colouring and Drying of Sheets of Paper, Cloth or the like (I p. 578).
Metallic Gloss Prints (IX p. 592).

XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

Swelling of Collagen and Modified Collagen. J. M. Cassel and E. McKenna. *J. Amer. Leather Chem. Assocn.*, **49**, 553–574 (Aug. 1954).

A detailed study is presented of the swelling in aq. media of collagen (hide powder) and of collagen modified by acetylation, deamination, esterification, and tanning with different concn. of HCHO, quinone, glyoxal, methyl glyoxal, Cr, Zr, quebracho, chestnut, and gambier. Some theoretical aspects of the tanning action which may occur are discussed on the basis of the swelling data presented. Swelling is measured in aq. media of pH 1·8–12·0, and is derived from the weight of the swollen material. Collagen tanned with HCHO resists swelling in either acidic or basic media; other tannages may suppress swelling in acid, but are less effective than HCHO in basic media. The swelling of collagen in aq. media is temp.-dependent; this dependence is most pronounced in media where Donnan equilibria and osmotic pressure are operative, e.g. pH 2 and 11·5. In water, measurable protein swelling is greater at 22° than at either 1° or 37°C. J. W. D.

Action of Carrotting Agents. E. H. Mercer. *J. Textile Inst.*, **45**, T 719–T 722 (Sept. 1954).

Experiments are carried out to determine whether carrotting produces in fur fibres a bilateral differentiation analogous to that which occurs in wool. Untreated and carrotted rabbit hairs are treated in reagents known to swell or supercontract keratin fibres, e.g. 0·1 N-NaOH, 90% phenol at 90°C., and boiling 0·01 N-HCl; the resulting slight curling of untreated hairs is greatly enhanced by carrotting, the effect being uneven but greatest on the tip halves. Birefringence studies show that bending is due to preferential expansion of unsymmetrically alkali-damaged fibres, and to preferential contraction of unsymmetrically acid-damaged fibre. Mercuric carrotting agents react with wool in a very markedly unsymmetrical fashion, the colour implying that complex tyrosine–metallic groups are involved. It is clear, therefore, that the agents do react asymmetrically with an already asymmetric fibre, and may thus enhance the relatively small asymmetry of rabbit hair. On the other hand, the mode of application of carrotting agents to fur is such that the fibres may be treated more liberally on one side than on the other. J. W. B.

Configuration of certain Protein Molecules. J. T. Edsall. *J. Polymer Sci.*, **12**, 253–280 (Jan. 1954).

The general size and shape of protein molecules in solution is correlated with knowledge of possible configurations of polypeptide chains and, in some cases, with the sequence of amino acid residues in these chains. The formation of helices and pleated sheets from polypeptide chains and the dimensions of these structures are discussed, and the possible significance of proline residues to bending and folding is indicated. Protein molecules are regarded as highly ordered and regular structures, but they are probably not completely rigid. Protein hydration is considered, and information regarding hydration and shape of protein molecules in solution from hydrodynamic measurements is critically discussed. Evidence available concerning shape and size of some well known proteins is examined, and future prospects of progress in this field are considered. W. R. M.

Anhydrous Trifluoroacetic Acid as a Solvent for Proteins. J. J. Katz. *Nature*, **174**, 509 (11 Sept. 1954).

The lower aliphatic perfluorocarboxylic acids, e.g. trifluoroacetic acid, possess solvent properties for proteins very similar to those of HF. Among the many dissolved are peanut protein globulin, casein, zein, silk fibroin, hide collagen, and rat-tail tendon. Solutions in the concentration range 20–30 mg./ml. are easily prepared at 25°C.; when prepared *in vacuo* they are clear and colourless. The protein can be readily recovered by direct evaporation or by lyophilisation. J. W. B.

Tanning Agents (III p. 579).

Metallic Gloss Prints (IX p. 592).

XIII—RUBBER; RESINS; PLASTICS

Effect of Compounds of Low Molecular Weight on the Deformation of Cellulose Nitrate over a Wide Range of Temperature. P. V. Kozlov and E. F. Russkova. *Doklady Akad. Nauk S.S.S.R.*, **95**, 583–586 (21 March 1954).

Cellulose nitrate (11·8% N, mean mol. wt. 115,000) is stirred with a soln. of plasticiser (camphor, diethyl phthalate, dibutyl phthalate, triphenyl phosphate, butyl stearate, or castor oil, the proportion varying from zero to 0·75–2 mol. per glucose residue) in methylene dichloride, and the material remaining after evaporation of solvent is compressed at 90°c. into a tablet (diameter 15 mm.), which is tested over a wide temp. range (20–150°c.) for deformation under a load oscillating between the limits of 85 and 1785 g. (100 oscillations per min.). In presence of non-compatible plasticisers (butyl stearate, castor oil), the cellulose nitrate remains in the glassy state, and the general effect of increased concn. or rise in temp. is merely to increase ease of deformation. The most notable effect of compatible plasticisers is to lower (to an increasing extent as the concn. rises) the temp. at which a change of state occurs. Some of the plasticisers (camphor, dimethyl phthalate) induce a change to the state of viscous flow (the initially almost horizontal deformation–temp. curve becomes almost vertical at a fairly well defined temp.). Others (dibutyl phthalate, triphenyl phosphate) may give rise to an intermediate elastic state of high deformability, which may pass at higher temp. into a state of viscous flow. The theoretical basis of the observed changes is discussed. A. E. S.

Kinetic and Thermal Study of the Polymerisation of 7-Heptanolactam. S. M. Skuratov, V. V. Voevodskii, A. A. Strepikheev, E. N. Kanarskaya, R. S. Muromova, and N. V. Fok. *Doklady Akad. Nauk S.S.S.R.*, **95**, 591–594 (21 March 1954).

Experiments similar to those previously described on the polymerisation of 6-hexanolactam in presence of varying amounts of water (see J.S.D.C., **69**, 99 (1953)) are now carried out for 7-heptanolactam, and give analogous results. The period of induction is somewhat shorter, and the max. rate of polymerisation is less (by ~30%) (at the same water content). The degree of conversion at which max. rate of polymerisation is attained is again independent of water content (30–32%; cf. 42% for 6-hexanolactam). The heat of reaction is 5·19 kcal./mole (cf. 3·26 kcal./mole for 6-hexanolactam), and the activation energy for the reaction is 23 kcal./mole. These further results enable refinements to be made in the theoretical treatment previously given for the polymerisation of lactams. A. E. S.

Acid Catalysis of the Polymerisation of 6-Hexanolactam. S. M. Skuratov, V. V. Voevodskii, A. A. Strepikheev, E. N. Kanarskaya, and R. S. Muromova. *Doklady Akad. Nauk S.S.S.R.*, **95**, 829–832 (1 April 1954). **Base Catalysis of the Polymerisation of 6-Hexanolactam.** Idem. *Ibid.*, **95**, 1017–1020 (11 April 1954).

The polymerisation of 6-hexanolactam is studied by the methods used previously (see previous abstract), a further component—butyric acid, phosphoric acid, butylamine, or caustic soda—being present in addition to water. Acids and bases do not catalyse the reaction when water is absent, but in its presence they reduce the period of induction and the total duration of the reaction, which reaches its max. velocity at 25–30% conversion when acids are present and at 45–50% conversion when bases are present (instead of 42% in absence of acid or base). The theoretical treatment is extended to include the effect of hydrogen and hydroxyl ions, and kinetic equations are derived that satisfactorily represent the observed behaviour. A. E. S.

Macromolecular Compounds. LXI—Decarboxylation of Dicarboxylic Acids during Polycondensation. V. V. Korshak and S. V. Rogozhin. *Izvestiya Akad. Nauk S.S.S.R., Otdel. khim. nauk*, 541–549 (May–June 1954).

Decarboxylation occurring in a mixture of a dicarboxylic acid (oxalic, malonic, succinic, adipic, or sebacic) and ethylene glycol is followed by measuring the carbon

dioxide formed, and the properties of any resulting macromolecular product are examined. The decarboxylation temperatures of the acids are greatly lowered by the presence of ethylene glycol, and as a result oxalic and malonic acids do not form macromolecular products and the molecular weights of the polyesters yielded by succinic and adipic acids fall rapidly with rise in condensation temp. Differences observed between the viscosimetric and end-group molecular weights of the polycondensates indicate a preponderance of hydroxyl over carboxyl end-groups, and, since the cyclic decarboxylation products of succinic and sebacic acids are considered to be incapable of taking part in the polycondensation reaction, decarboxylation must occur mainly at terminal acid residues, the carboxyl at the end of a macromolecule being, therefore, less stable than a carboxyl of the free acid. A. E. S.

Polymerisation of Acrylics. I— Chemistry of Polymerisation of the Acrylics. II— Acrylonitrile Copolymers and Relationship to Dyeability. G. E. Ham. *Text. Research J.*, **24**, 597–604, 604–614 (July 1954).

I— The methods of polymerisation of acrylonitrile are discussed and the catalysts employed are reviewed. The mechanism of polymerisation and the relationship between molecular weight, chemical structure, and fibre properties are detailed.

II— Dyeability of acrylonitrile compositions with acid dyes is correlated with the basic monomer structure. The copolymerisation characteristics of acrylonitrile with certain basic monomers are discussed. Aminated methyl vinyl ketone copolymers, alkyl glycidyl ether copolymers, and methallyl chloroacetate copolymers are considered.
A B

Some Applications of Organic *iso*Cyanates (III p. 579).
Rendering Commercially Purified Acrylonitrile Colourstable (VI p. 589).

XIV— ANALYSIS; TESTING; APPARATUS

Titration of Calcium with Ethylenediaminetetraacetate in the Presence of Magnesium. R. D. Bond and B. M. Tucker. *Chem. and Ind.*, 1236–1237 (2 Oct. 1954).

In the joint titration of Mg and Ca with disodium ethylenediaminetetra-acetate, using murexide as indicator, the control of pH is very important; this is increasingly so the greater the ratio of Mg to Ca. The effect is attributed to the adsorption of Ca on the $Mg(OH)_2$ ppt. at excessive alkalinities. Three methods are recommended and described for the determination of Ca and Mg in soln. containing no interfering ions; the first is generally applicable, the second is particularly useful for natural waters and other unbuffered soln., and the third is especially applicable to the titration of Ca in NH_4Cl extracts.
J. W. D.

Quantitative Infrared Analysis of Mixtures. I. R. C. McDonald. *Nature*, **174**, 703–704 (9 Oct. 1954).

The use of a double-beam infrared spectrophotometer in the differential analysis of complex mixtures of isomeric or closely related substances in solution, is described. Methods are given for the elimination of interferences due to absorption by solvents and/or other substances. The determination is described of *trans* unsaturated fatty acids in presence of *cis* unsaturated fatty acids and saturated fatty acids, and of a mixture of the *pp'* and *oo'* isomers of DDT, and the γ isomer of BHC (benzene hexachloride). The method may also be used as a criterion of purity.
J. W. D.

Adsorption Columns in the Analysis of Emulsions stabilised with Non-ionic Detergents. T. Green, R. P. Harker, and F. O. Howitt. *Nature*, **174**, 659 (2 Oct. 1954).

Emulsions containing lanolin (I), Lissapol N (II), and up to 1% NaCl are resolved on columns of Bio-Deminrolit (an intimate mixture of Zeokarb 225 and De-Acidite FF); the emergent liquid is clear, and leaves no residue on evaporation. Elution with ethanol affords quant. recovery of II, and I may be similarly removed by trichloroethylene. The mixed resin first breaks the emulsion by removal of the stabilising electrolyte, before adsorbing the grease and the detergent. Emulsions of II with mineral or vegetable (olive) oil have been similarly resolved and estimated. In the analysis of an emulsion containing I, II, and soap, II is removed as above, on a column of Bio-Deminrolit, and eluted with 50% aq. ethanol; soap and I are separated on a column of Zeokarb 225 and charcoal, the latter retaining I strongly whilst the soap and grease components are eluted.
J. W. D.

New Micro Method for the Analysis of Phenols. B. T. Commins and R. L. Cooper. *Chem. and Ind.*, 1110 (4 Sept. 1954)

The mixture containing phenols is methylated, and the ethers so formed are chromatographed on a column of activated alumina (or, if phenols alone are present, silica), *cyclo*hexane being used as solvent; the column eluates are examined spectroscopically. The ethers formed from a mixture of mono- and poly-hydric phenols separate out according to molecular complexity and the number of methoxy groups, the latter factor predominating: the most complex ethers enter the filtrate last. The method, which requires only a few μg. of the phenol(s), is more rapid, precise, and specific than either the Gibbs test or paper-chromatographic methods. J. W. D.

Qualitative and Quantitative Analysis of Vat Dyes by Paper Chromatography. E. Klingsberg. J.S.D.C., **70**, 563–567 (Dec. 1954).

By operating in an atmosphere of nitrogen, it has been found possible to effect chromatographic separations of vat dyes in leuco form on strips of paper or synthetic fibres. The technique has been applied to the quantitative analysis of model mixtures, employing spectrophotometric determination of the individual constituents after their chromatographic isolation from the mixture. AUTHOR

Identification of Azo Dyes by Spectrophotometric Identification of their Reduction Products. II— Compounds which give Neutral or Acidic Products on Reduction. L. S. Harrow and J. H. Jones. *J. Assoc. Offic. Agr. Chemists*, **36**, 914–923 (1953): *Chem. Abs.*, **48**, 9693 (25 Aug. 1954).

Procedures, practical examples being given, applicable to samples containing only a few mg. of azo dye for separation and spectrophotometric identification of the water-soluble neutral and acidic compounds obtained by reducing the dye. C. O. C.

Separation of Certain Anthraquinone Dyes by Paper Chromatography. L. C. Mitchell. *J. Assoc. Offic. Agr. Chemists*, **36**, 943–6 (1953): *Chem. Abs.*, **48**, 9693 (25 Aug. 1954).

Mixtures of three water-soluble and two water-insoluble anthraquinone dyes were separated in one step by paper chromatography. The paper used was prepared by spraying it with an ether solution of the stationary phase (soya-bean oil). The mobile phase was Methyl Cellosolve and water (4 : 1). C. O. C.

Coal-tar Colours. XIII— D&C Red No. 33. R. N. Sclar. *J. Assoc. Offic. Agr. Chemists*, **36**, 930–6 (1953): *Chem. Abs.*, **48**, 9694 (25 Aug. 1954).

Describes preparation, analysis and optical properties of pure D&C Red No. 33 and Chromotrope 2R, together with a paper-chromatographic method for determining Chromotrope 2R in commercial D&C Red No. 33.
C. O. C.

Report on Paper Chromatography of Coal-tar Colours. D. H. Tilden. *J. Assoc. Offic. Agr. Chemists*, **36**, 802–810 (1953): *Chem. Abs.*, **48**, 9694 (25 Aug. 1954).

Continuation of previous work. Only two replies were received on the three collaborative FD&C dyes.
C. O. C.

Report on Subsidiary Dyes in D&C Colours (4-Tolylazo-2-naphthol in D&C Red No. 35). L. Koch. *J. Assoc. Offic. Agr. Chemists*, **36**, 796–8 (1953): *Chem. Abs.*, **48**, 9695 (25 Aug. 1954).

Results from 5 analysts confirm that the proposed method of determining the subsidiary dye is satisfactory.
C. O. C.

Report on Boiling Range of Amines derived from Coal-tar Colours. Xylidine from FD&C Red No. 32. L. S. Harrow. *J. Assoc. Offic. Agr. Chemists*, **36**, 795–6 (1953): *Chem. Abs.*, **48**, 9695 (25 Aug. 1954).

Wide variations have been obtained by different analysts using the A.O.A.C. method for determining the boiling range of pseudocumidine as a method for determining the boiling range of xylidine obtained by reducing FD&C Red No. 32. C. O. C.

Separation and Determination of Sulphonated Naphthalene Intermediates in Certifiable Coal-tar Colours. L. S. Harrow and K. S. Heine. *J. Assoc. Offic. Agr. Chemists*, **36**, 936–943 (1953): *Chem. Abs.*, **48**, 9695 (25 Aug. 1954).

Column chromatography followed by ultraviolet spectrophotometric determinations is relatively rapid and simple. It gave accurate and reproducible results when determining 5 sulphonated naphthalene derivatives in several certifiable coal-tar dyes. The same method renders possible determination of similar compounds in other dyes and of individual sulphonated naphthalene derivatives in certain mixtures. C. O. C.

Report on Lower-sulphonated Dyes in FD&C Blue No. 1. M. Dolinsky. *J. Assoc. Offic. Agr. Chemists*, **36**, 798–802 (1953): *Chem. Abs.*, **48**, 9695 (25 Aug. 1954).

Study of methods of determining lower-sulphonated dyes in FD&C Blue No. 1 which has led to recommendation of a method for further study. C. O. C.

Paper-chromatographic Separation of Artificial Colouring Materials in Preserves. J. J. Monselise and D. Miranda. *Inds. agr. et aliment.* (Paris), **71**, 223–4 (1954): *Chem. Abs.*, **48**, 9581 (25 Aug. 1954).

Extract the colouring material by several adsorptions on wool, elute with ammonia, boil and make slightly acid with H_2SO_4 and chromatograph on paper. After complete adsorption of the colouring material, dry the chromatogram and develop it with ethyl alcohol (9 parts) and water (1) and identify each material by its specific reactions. The chromatogram paper is impregnated with $CaCO_3$ by successive treatments with $CaCl_2$ and $(NH_4)_2CO_3$ and thoroughly washed free from $CaCl_2$. C. O. C.

Colorimetric Evaluation of Rutin and Quercetin from their Degradation Products. M. Zafix. *Folia Pharm.* (Istanbul), **3**, 9–13 (1954): *Chem. Abs.*, **48**, 9277 (25 Aug. 1954).

Controlled oxidation of rutin with $KMnO_4$ yields 2:4-dihydroxybenzoic acid, which can be determined colorimetrically by addition of aq. $FeCl_3$.

To 0·2 g. rutin (dried over $CaCl_2$) in a 200 c.c. beaker add 50 c.c. N-NaOH, heat to boiling, then slowly add while warming and stirring 1 g. $KMnO_4$ in 20 ml. water, cool, filter, wash with warm water until the filtrate amounts to 80 ml., neutralise with 10 c.c. 36% HCl in 20 c.c. distilled water until the pH is 2 and dilute to 100 ml. To 1 c.c. of this solution add one drop of 10% aq. $FeCl_3$ to yield an orange–brown solution which is read directly in the colorimeter as rutin. The method is sensitive to 0·2 g. rutin per 200 c.c. solution. C. O. C.

Use of Alkali and Aluminium Chloride in the Spectral Study of Phenolic Plant Pigments. J. B. Harborne. *Chem. and Ind.*, 1142–1143 (11 Sept. 1954).

The identification of unknown phenolic plant pigments, such as *iso*flavones, anthocyanins, and aurones, is often greatly assisted by a study of their spectra in neutral and alkaline soln., and by observation of the spectral shift resulting from the addition of $AlCl_3$ to the soln. Numerous examples are tabulated and discussed. J. W. D.

Optical Evaluation of Pigments. I— Discussion and Methods. II— Whites, Yellows, and Bright Reds. M. H. M. Arnold. *J. Oil & Col. Chem. Assocn.*, **37**, 508–512, 513–518 (Sept. 1954).

I— The essential properties of a pigment are opacity and colour; both contribute to the hiding power of a paint, but by different mechanisms, and must therefore be separated for a fair evaluation. The quant. estimation of colour (as tinting strength) is well developed. Colour in paint requires opacity for its disclosure; this may be supplied in the same pigment or separately. True opacity is due entirely to reflection, and is unrelated to tinting strength; knowledge of one does not, therefore, confer knowledge of the other. There is no universally accepted method for determining opacity. A simple method is described for determining the opacity of a pigment independently of its colour, in which 1 g. of the pigment under test is rubbed out in refined linseed oil, and Drop Black is rubbed in until the colour matches that of a standard, based on rutile TiO_2 and Drop Black. The opacity is quoted in terms of grams of black added per 100 g. of pigment, and the cost of opacity is the cost in pence per lb. of the pigment divided by the opacity as determined above. The examination of white pigments is straightforward, but with other colours undertone effects often interfere seriously. With yellows and bright reds it has been found possible to make satisfactory determinations by using yellow or red (dark-room) light respectively. This method may be further extended by selection of appropriate light filters for other colours such as crimsons, bordeaux, maroons, greens, and blues.

II— A large number of white, yellow, and bright red pigments have been evaluated by the method described above. The order of opacity of white pigments agrees with that generally accepted. The most opaque yellows, on a weight basis, are the Hansa Yellows, but the lead chromes are clearly the most opaque on a cost-of-opacity basis. For self-colour red paints, two very different types of bright red pigment are required: a high-opacity permanent pigment whose cost is not of prime importance, and a high-opacity cheap pigment whose permanence is not vital. For the first purpose the Helio Reds are outstanding, but no cheap organic reds of high opacity appear to exist, and the second purpose can be served only by molybdated chromes, tinted, since their colours lie towards the orange, by relatively transparent bluish-red toners. The opacities, tinting strengths, and prices of numerous pigments are tabulated. J. W. D.

Determination of Zinc in Paint Pigments. G. Damany. *Peintures, Pigments, Vernis*, **29**, 995–996 (1953): *Chem. Abs.*, **48**, 11078 (25 Sept. 1954).

Critical study of methods for determining Zn in pigments showed the electrolytic method to be best. The pigment is decomposed in boiling 0·5N-HCl, filtered, and washed with 0·1N-HCl. The filtrate is neutralised with ammonia and KCN and excess ammonia added. The Zn is deposited electrolytically on tared Cu electrodes and the deposit weighed. C. O. C.

Identification of Textile and Related Fibres. J. E. Ford and W. J. Roff. *J. Textile Inst.*, **45**, T 580–T 623 (Aug. 1954).

A comprehensive yet simple scheme is presented for the identification of textile fibres. First the fibres are classified, by means of a microscope, (*a*) as natural and (*b*) as man-made; each group is then separated into six subgroups (*a*) by morphological differences and (*b*) by thermoplasticity and presence of Cl or N. Final identification is completed by chemical tests. A total of approx. 40 natural and 30 man-made fibres are considered, with inclusion of 64 photomicrographs. J. W. B.

Fugitive Tinting. W. Meitner and J. E. Taylor. *J. Textile Inst.*, **45**, P 369–P 379 (Aug. 1954); *Colour and Textiles* (*Proc. Joint Conference*), pp. 29–39.

Fugitive tints must be readily removable by scouring, they must be fast to light and heat, they must not migrate, and they should be available over a good colour range. These properties and the shortcomings of available tints are discussed with reference to viscose and cellulose acetate rayons, wool, and nylon, under the headings of pigments, normal dyes, and high polymer–dye complexes, with a special section on casein–dye complexes. J. W. B.

Chemical Methods for the Analysis of Cotton–Viscose Rayon Mixtures. G. Cuvelier, A. Caille, and M. Aubry. *Bull. Inst. Text. France*, (45), 65–74 (April 1954).

The effect on cotton of reagents used to dissolve viscose rayon in four analytical methods is studied. Samples of cotton fibres from six different sources were used, and the loss in wt. was determined on raw, scoured, bleached, and mercerised samples. The sodium zincate method gives the best results, since it has the least effect on the cotton. Purification of samples before analysis by means of a mild scour in Na_2CO_3 soln. is desirable, particularly for mixtures containing raw cotton. When the rayon content of mixtures is less than 10%, chemical methods of separation are not accurate. G. L.

Chemical and Physical Research Methods for Viscose Rayon Filaments. J. Pinto. *Bull. Inst. Text. France*, (45), 7–30 (April 1954).

A summary of physical and chemical methods which can be used for the study of defects in viscose rayon fabrics. G. L.

Comparison of the Sulphuric Acid and Sodium Hydroxide Methods for analysing Wool mixed with Cotton and Viscose Rayon. E. Horowitz and J. Mandel. *Amer. Dyestuff Rep.*, **43**, 613–615 (13 Sept. 1954).

The H_2SO_4 and NaOH methods of separating wool from cotton and/or viscose rayon are compared with respect to their suitability for the analysis of low concentrations of wool in presence of other fibres. It is shown that a single determination of wool content by either method gives a result within 1% of wool when present from 5 to 25%, the standard deviations being 0·28% by the acid method and 0·37% by the alkali procedure. Results by NaOH are on the average low by 0·6% for wool–cotton and 0·1% for wool–cotton–viscose rayon. These values are independent of the % of wool and are, therefore, of greater significance when the proportion of wool is low. By the H_2SO_4 method the results are high by 1·7 and 1·0% respectively, this error depending on the amount of wool, perhaps owing to traces of H_2SO_4 retained in the residue. Removal of size is more important in the NaOH method because this determines the wool indirectly. A 2-g. sample is suitable in either method. J. W. B.

Bilateral Asymmetric Deposition of Gold in Wool Fibres. G. Laxer and D. A. Ross. *Text. Research J.* **24**, 672–674 (July 1954).

It is shown that treatment of a highly crimped wool fibre with a soln. of gold chloride can result in an asymmetrical deposition of coarse, black metallic gold particles in the cortex, and that this deposition can be correlated with the crimp of the fibre. A. B.

Chromatographic Separation of the Diastereoisomerides of Lanthionine—Determination of Lanthionine. S. Blackburn and G. R. Lee. *Chem. and Ind.*, 1252 (9 Oct. 1954).

The soln. containing lanthionine (I) is applied to a column of Dowex 50 by the method of Moore and Stein (*J. Biol. Chem.*, **192**, 663 (1951)). The column is developed with the pH 3·42 buffer only, and the eluate is collected in 1-ml. fractions. Ninhydrin is used to determine I (which emerges from the column in the region between serine and glutamic acid), the developed colour being measured spectrophotometrically at 455 mμ. Optical density and concn. of I are linearly related up to 45 μg./ml. Proline and lysine emerge from the column later than I, and thus do not interfere, although they, too, develop colours with ninhydrin. The L and *meso* forms of I are completely separated by the use of favourable column conditions, but the L and D forms are not. The procedure is described in full. Similar separations of the diastereoisomerides of hydroxylysine, *iso*leucine, hydroxyproline, and threonine have also been reported, and the method has been applied to the analysis of wool keratin which has been treated with alkali under different conditions. J. W. D.

Determining the Proportion of Acetate Rayon in Mixtures with Cotton. F. di Stefano and F. Muntoni. *Rend. Ist. super. Sanità*, **17**, 55–8 (1954): *Chem. Abs.*, **48**, 9696 (25 Aug. 1954).

The sample is heated with a mixture of acetic and nitric acids. This dissolves out all the acetate rayon without affecting the cotton. C. O. C.

Action of Zinc Chloride–Iodine Solution on Synthetic Fibres. Reaction for Distinguishing between these Fibres. B. Hauptmann. *Deut. Textilgewerbe*, **53**, 156–9 (1951): *Chem. Zentr.*, **1**, 3585 (1951): *Chem. Abs.*, **48**, 9698 (25 Aug. 1954).

Nylon, Perlon L, Perlon U, Orlon and Terylene are placed on a microscope slide, a drop of 20% aq. phenol added and heated. Terylene shrinks 20% in length while Orlon remains unaltered in length; neither is dissolved. Perlon L dissolves most readily, then nylon, and lastly Perlon U. $ZnCl_2$–I_2 solution also enables recognition of the various fibres according to whether or not they dissolve. Numerous photomicrographs are given illustrating the swelling of the fibres. C. O. C.

Classifying Detergents. J. V. Karabinos, G. E. Kapella and G. E. Bartels. *Soap & Chem. Specialties*, **30**, (6), 41–3 (1954): *Chem. Abs.*, **48**, 9085 (10 Aug. 1954).

The following six tests are proposed for classifying the various types of anionic and non-ionic detergents—(*a*) the $Ce(NO_3)_4$ test for OH groups, (*b*) colour produced on $AlCl_3$ in $CHCl_3$, (*c*) bromine water test for alkylphenol ethers, (*d*) $KMnO_4$ test for unsaturation, (*e*) alcoholic KOH test for esters, and (*f*) a modified Liebermann–Storch test for rosin derivatives. Results obtained with many organic detergents are tabulated. C. O. C.

Detergent Efficiency—Interpretation of Reflectance Curves. O. C. Bacon and J. E. Smith. *Amer. Dyestuff Rep.*, **43**, P 619–P 622 (13 Sept. 1954).

The relative efficiencies of detergents for removing soil are obtained directly from reflectance data, the method being based on the difference in mechanical work required to give the same results with various detergents when all other washing conditions are maintained constant. The same principles can be used to determine the relative efficiencies of washing machines and the effects of temperature, water hardness, and detergent builders. The method applies to any soil-removal measurements provided that the reflectance changes can be assessed, the removal is below 90–95%, and mechanical action is required for the removal. The formula employed is—

$$\text{Relative efficiency} = \text{Antilog}\ \frac{R_2 - R_1}{33{\cdot}2b}$$

(R_2 and R_1 = two reflectivity readings relative to MgO; b = an experimentally obtainable constant). J. W. B.

Detergent Performance Evaluation. J. C. Harris, M. R. Sullivan, and L. E. Weeks. *Ind. Eng. Chem.*, **46**, 1942–1947 (Sept. 1954).

In detergency testing by the washing of artificially soiled patterns, the percentage soil removal is often calculated on reflectance measurements, based on the fallacious assumption that the light absorbed by a soiled fabric is directly proportional to the concentration of carbon or graphite present. A method has been devised for the removal of graphite from cotton cloth and its turbidimetric determination, with a max. error of ±6·5%. This has enabled a direct comparison to be made between reflectance value and actual graphite content, and it is shown that the relationship is of the type—

$$R = -A \log G + B$$

(R = reflectance; G = concn. of graphite; A and B = constants). The Kubelka–Munk equation—

$$\frac{K}{S} = \frac{(1-R)^2}{2R}$$

(K = coefficient of reflectivity; S = coefficient of light scattering; R = observed reflectivity for monochromatic light) relating reflectance to soil concentration has been verified experimentally, and the K/S value for colloidal graphite on cotton fabric is shown to be essentially a linear function of graphite concentration. W. K. R.

Determination of Vat Dyes on Wool. N. G. Klemin, P. V. Moryganov, and A. A. Solov'ev. *J. Appl. Chem. U.S.S.R.*, **27**, 797–800 (July 1954).

Vat-dyed wool (0·1 g.) is dissolved in conc. H_2SO_4 (10 ml.) at 110°C. (5 min.). The soln. is cooled and added slowly with agitation and cooling to 70 ml. of a 0·1% aq. soln. of gelatin or Peregal. The dye sol so obtained is made up to 100 ml. with the same soln. and is compared colorimetrically with sols prepared similarly from the appropriate amount of undyed wool and known amounts of the vat dye.

A. E. S.

Use of Fading Lamps for Determining Light Fastness. K. McLaren. J.S.D.C., **70**, 553–556 (Dec. 1954).

There are three possible causes of the significant differences sometimes experienced between fading-lamp and daylight fastness figures—spectral composition, temperature, and moisture content. Although there are marked differences between the spectral composition of fading lamps and sunlight, on theoretical grounds these would not appear to be the main cause of large discrepancies. The most likely cause is surface moisture content during exposure, and this depends on surface temperature and on the relative humidity of the surrounding air. It will be necessary to investigate these factors in detail before a specification for fading-lamp operation can be issued.

AUTHOR

Effects of Temperature and Humidity on the Light Fastness of Dyed Synthetic Fibres in the Fade-Ometer. AATCC Mid-West Section. *Amer. Dyestuff Rep.*, **43**, P 497–P 505 (2 Aug. 1954).

Two groups of fibres are studied—(1) those which can be dyed with disperse dyes, viz. acetate rayon, Terylene, dynel, Orlon, and nylon; and (2) those which can be dyed with acid dyes, viz. nylon, Acrilan, Vicara, and wool. More than 1300 samples are exposed, at 135°, 155°, and 175°F. and 35, 50, and 65% R.H. Results indicate that temperature affects fading more than does R.H., and suggest that fibre grouping gives more definite patterns than does dye grouping.

J. W. B.

New Recommended Test Conditions and Operating Practices for Light Fastness Tests in the Fade-Ometer. J. E. Norton. *Amer. Dyestuff Rep.*, **43**, P 628–P 631 (13 Sept. 1954).

The AATCC Standard Sun Test does not always give the same result when compared with the blue wool light-fastness standards; this is due to variations in conditions, particularly the temperature of the specimen. Directions are given for correct Fade-Ometer operation, by means of which correlation with properly conducted sun tests will be very good.

J. W. B.

Rapid Test for Gas-fading Resistance of Dyed Cellulose Acetate Fabrics. H. M. Friedman. *Amer. Dyestuff Rep.*, **43**, 597–598 (30 Aug. 1954).

A pint jar containing 1 g. $NaNO_2$ in 250 ml. water at 40°C. is placed inside a 15-litre glass bottle, in the cap of which is fitted an arrangement for suspending small pieces of test fabric, and a funnel and tube leading into the nitrite solution. With the fabric and cap in position, 50 ml. of water containing 5 g. of conc. HCl is poured in, and the time taken for the sample to fade to a standard is recorded. Results obtained on fabrics treated with fading inhibitors suggest that the method is suitable as a spot test.

J. W. B.

Specification and Labelling of Colour Fastness for the Consumer. J. A. van der Hoeve. *J. Textile Inst.*, **45**, P 415–P 426 (Aug. 1954); *Colour and Textiles* (*Proc. Joint Conference*), pp. 75–86.

The advantages, disadvantages, and practicability of colour-fastness labelling are discussed, consideration being given to the customers' views, the intended use of the fabric, and the influence of fashion. Classes of dyes available, the choice of dyes within the classes, the performance of the dyes, the influence of the dyeing method and of the finish—all provide technical limitations for the dyer. An international system is favoured, but requires that universal standards of fastness testing should be established.

J. W. B.

Effect of Background on Colour Discrimination. G. N. Rautian and V. P. Solov'eva. *Doklad§ Akad. Nauk S.S.S.R.*, **95**, 513–516 (21 March 1954).

Colour discrimination tests are made within a central field of 4°, which is viewed on a background of at least 60°. The field and the background have identical or contrasting specified hues (including white), which are varied in intensity. The results are expressed in the form of threshold ellipses on a tristimulus chromaticity diagram, and they show that colour discrimination is not greatly affected by the character of the background (the axes of the threshold ellipse may increase to about three times their optimum values when a very intense background of contrasting hue is present). Discrimination is generally at its best when field and background are identical in hue and intensity; blue forms an exception, optimum conditions being obtained when the background is black.

A. E. S.

Effect of Level of Illumination on Colour Discrimination. G. N. Rautian and V. P. Solov'eva. *Doklad§ Akad. Nauk S.S.S.R.*, **95**, 1189–1192 (21 April 1954).

Colour discrimination tests are made for a field (one of seven colours or white) of variable luminosity, and it is found that discrimination becomes poor (threefold increase in discrimination threshold) at a luminosity of $2–10 \times 10^{-5}$ stilb, and a state of virtual colour blindness (20-fold increase in threshold) is reached at $2–3 \times 10^{-6}$ stilb. At this level of illumination vague changes in blueness and redness can be observed, but all appreciation of greening has disappeared. For luminosities of $> 3 \times 10^{-4}$ stilb, the variation in colour discrimination with illumination can be neglected for practical purposes.

A. E. S.

Analytical Total Acid Hydrolysis of Dextrans. R. J. Dimler, H. A. Davis, G. J. Gill, and C. E. Rist. *Anal. Chem.*, **26**, 1142–1146 (July 1954).

Studies of the hydrolysis of dextran (I) and destruction of D-glucose (II) under a limited range of hydrolysis conditions show that, within the limitations of the measurements, essentially the same max. yield of reducing sugars and concurrent loss of II were obtained with 2 and 4 N-H_2SO_4 and 1 and 2 N-HCl at 100°C., and N-H_2SO_4 at 120°C., the point of max. yield being reached in times ranging from 50 to 180 min. In terms of normality, HCl is ca. twice as effective as H_2SO_4. A standardised procedure is given for the analytical hydrolysis of I, employing a 0·5% soln. of I in 4 N-H_2SO_4 heated at 100°C. for 75 min., the reducing power being corrected for an approx. 4% loss of II during hydrolysis. The applicability of the procedure to different types of dextran is demonstrated.

J. W. D.

Standard Methods for the Removal of Added Matter from Textiles. *J. Textile Inst.*, **45**, s 37–s 49 (Sept. 1954).

Standard procedures are described for removing sizes, etc. from cotton, viscose rayon staple, linen, jute, cellulose acetate rayon, continuous-filament viscose rayon, cuprammonium rayon, spun and nett silk, wool, nylon, Terylene, Orlon, and Ardil. Detailed methods are also presented for removing amino–formaldehyde resins, bitumen, gelatin, cellulose nitrate and polyvinyl chloride (from leathercloth), mineral khaki, naphthenates, oils, oleates, rubber coatings, tin weighting, and Willesden proofing.

J. W. B.

Permanent Protection of Cellulosic Materials against Micro-organisms. C. Zuber and L. Marcou. *Bull. Inst. Text. France*, (47), 69–93 (June 1954).

Standardised testing methods and application techniques for proofed fabrics are summarised. Chemicals used include phenolic derivatives, quaternary ammonium salts, metal complexes of organic substances, and Cu salts.

G. L.

Determination of Functional Groups in Tannins and Lignins. I— Determination of Hydroxyl Groups. W. E. Hillis. *J. Soc. Leather Trades Chem.*, **38**, 177–183 (June 1954); **II— Methylation Studies.** *Idem., ibid.*, **38**, 209–214 (July 1954).

I— A method for determining total hydroxyl content of the components of tannins and lignins entails acetylation with acetic anhydride and pyridine for several days at room temperature, hydrolysis of excess acetic anhydride with cold water, and electrometric determination of the acid. By this means 99·7% of the OH groups in pyrogallol, 99·0% in phloroglucinol, 98·8% in eugenol, 98·0% in catechin, and 100·4% in aromadendrin are estimated. Vanillin gives variable, and different lignin fractions consistent, results.

II— The concept that diazomethane will methylate always and only OH groups of an acidic nature is unreliable, and the use of alkali during the methylation is inadvisable, as the methylated products may be ruptured and new phenolic hydroxyls liberated. Studies on dihydrokaempferol, catechin, and lignin show that the choice of solvent can play a part during methylation. The relative solubilities of the components of lignin are changed during methylation, indicating that the methyl content of a methylated heterogeneous material must be accepted with reserve. J. W. B.

Application of Rhodamine B to Interaction Studies in Proteins and Simple Model Systems. H. P. Lundgren and C. H. Binkley. *J. Polymer Sci.*, **14**, 139–158 (Aug. 1954).

Using Rhodamine B as an indicator, the relative acidities of some phenols and alcohols as model hydrogen donors are determined in toluene solution, the method involving measurement of the change from colourless Rhodamine to the coloured form produced by the hydrogen donor. The method is applied to the determination of equilibrium constants for interaction of phenol with dimethylformamide, benzyl acetate, and dioxan. Results are in agreement with those of Flett (J.S.D.C., **68**, 59–64 (1952)). Partition of the dye between toluene and water is considered, forces tending to bind the dye in one phase decreasing its activity in that phase. Incorporation of propiolactone polymer into the wool fibre reduces the activity of dye in fibre in relation to non-polar as well as aqueous solutions, and the modified wool exhibits improved dyeing properties. The dye is useful for determination of the critical micelle concentration of fatty acid soaps in aqueous solution. It also shows markedly increased binding by heat-denatured as compared with native egg albumen and by acetylated, as compared with normal, wool. W. R. M.

Thixotropy, and Methods for its Measurement in Liquid-Plastic Colloidal Systems. A. A. Trapeznikov and V. A. Fedotova. *Doklady Akad. Nauk S.S.S.R.*, **95**, 595–598 (21 March 1954).

Rapid Determination of Combined Formaldehyde in Cellulose. T. N. Kleinert. *Melliand Textilber.*, **35**, 868–870 (Aug. 1954).

The material is hydrolysed with 85% phosphoric acid containing 0·05% chromotropic acid, pigments are filtered off if necessary, and the filtrate is analysed colorimetrically. S. R. C.

Flame-photometric Determination of Rubber Solids deposited on Cords and Fabrics. H. E. Todd and H. M. Tramutt. *Anal. Chem.*, **26**, 1137–1140 (July 1954).

The latex pick-up of natural or synthetic fibres may be measured by digesting the material in conc. HNO_3 and determining its Na content by flame photometry. The method is more rapid, of greater accuracy, and of wider applicability than others in current use. The method is described fully, and comparative analyses are cited. J. W. D.

Cadmium Pigments (IV p. 583).
Swelling of Hair and a Viscose Rayon Monofil in Aqueous Solutions (VI p. 587).
Effect of Water Vapour on Wool (VI p. 588).
Realisable Colour Gamuts in Dyeing (VIII p. 590).
Influence of the Substrate upon the Light Fading of Azo Dyes (VIII p. 590).
Measurements of Redox Potential in Continuous Vat Dyeing (VIII p. 591).
Some Factors in the Measurement of Affinities of Vat Dyes for Cellulose (VIII p. 591).
Dyeing of Cellulose Acetate from the Vapour Phase (VIII p. 591).
Moisture Regain and Accessibility of Cellulose Derivatives (XI p. 594).
Hydrolysis of Cellulose Acetate Sulphate in Acetone (XI p. 594).

XV— MISCELLANEOUS

Progress in Colloid Chemistry. J. A. Kitchener. *J. Oil & Col. Chem. Assocn.*, **37**, 355–377 (July 1954).

A review of the present state of progress in this field under the following broad headings— classification of colloids, soln. of macromolecules, aggregation colloids, and lyophobic colloids. There are numerous references to cellulose, proteins, synthetic polymers, and dyes. J. W. D.

Patent Protection in the Soviet Zone of Germany. K. Herbert. *Textil-Praxis*, **9**, 879–880 (Sept. 1954).

PATENT

White Shoe Dressings. Robinson & Groom. *BP* 715,250

A white shoe dressing resistant to rain consists of an aqueous dispersion containing a pigment, sulphonated castor oil (< 20% by wt. of the pigment), HCHO, sodium silicate and a water-soluble cellulose ether, the amount of each of the last three ingredients being less than that of the sulphonated oil. C. O. C.

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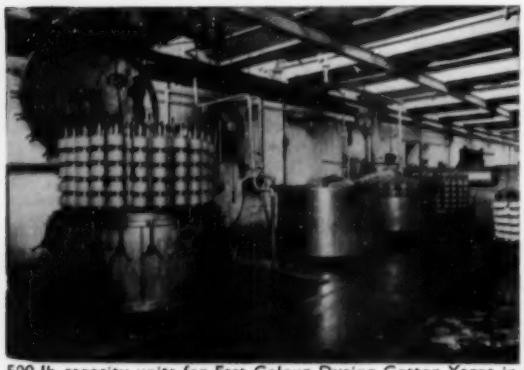

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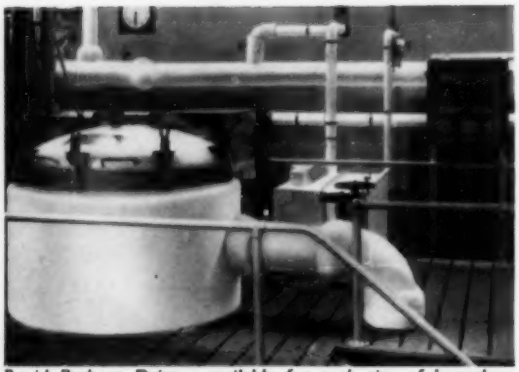

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FORTHCOMING MEETINGS OF THE SOCIETY — *continued from page* xii

Tuesday, 15th March 1955

HUDDERSFIELD SECTION. *Sulphur Colours for Special Purposes.* H. Senior, Esq. (James Robinson & Co. Ltd.). Preceded by Annual General Meeting, Princess Cafe, **Huddersfield.**

LEEDS JUNIOR BRANCH. *The Classification of Dyes by their Dyeing Characteristics.* W. Beal, Esq., B.Sc. (The Geigy Co. Ltd.). Departmental Lecture Theatre, The University, **Leeds.** 3.30 p.m.

SCOTTISH SECTION — LADIES' EVENING. *The Hand Printing of Textiles.* E. S. Beton, Esq. (Brocklehurst, Whiston Amalgamated Ltd.). Institution of Engineers & Shipbuilders, **Glasgow.** 7 p.m.

Thursday, 17th March 1955

BRADFORD JUNIOR BRANCH. *Dyeing and Finishing of Acetate Woven and Knitted Fabrics.* R. J. Mann, Esq., B.Sc. (British Celanese Ltd.). **Bradford** Technical College. 7.15 p.m.

Friday, 18th March 1955

MANCHESTER SECTION. One Day Symposium. Full details later.

Thursday, 24th March 1955

WEST RIDING SECTION — ANNUAL GENERAL MEETING. The Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Tuesday, 5th April 1955

SCOTTISH SECTION — ANNUAL GENERAL MEETING. 7 p.m. *Primitive and Modern Dyeing Practice.* (Illustrated) (I.C.I. Ltd.). St. Enoch Hotel, **Glasgow.** 7.30 p.m.

Wednesday, 6th April 1955

MIDLANDS SECTION. Paper by G. H. Lister, Esq., B.Sc., Ph.D. (Subject later) (ANNUAL GENERAL MEETING at 6.30 p.m.). Kings Head Hotel, **Loughborough.**

Friday, 15th April 1955

MANCHESTER SECTION — ANNUAL GENERAL MEETING. *The Dyeing of Acetate T.P.S. Fibre.* J. Boulton, Esq., M.Sc. Tech., F.S.D.C., F.T.I. 7 p.m.

Thursday, 21st April 1955

MIDLANDS SECTION. *Some Experiences of a knitted-goods dyer.* A. W. Carpenter. (Joint Meeting with the Textile Institute Kidderminster Section). Carpet Trades Canteen. Mill Street, **Kidderminster.** 7 p.m.

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The engagement of persons answering these advertisements must be made through a Local Office of the Ministry of Labour or a Scheduled Employment Agency if the applicant is a man aged 18–64 inclusive or a woman aged 18–59 inclusive unless he or she, or the employment, is excepted from the provisions of the Notification of Vacancies Order 1952.

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THE SOCIETY OF DYERS AND COLOURISTS

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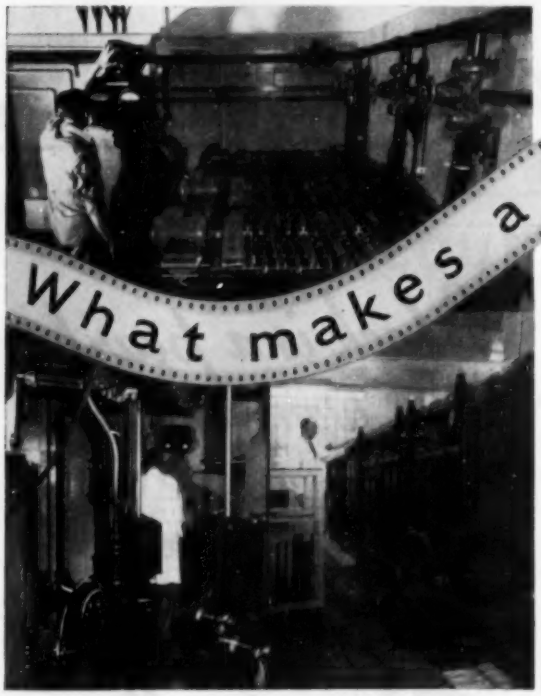

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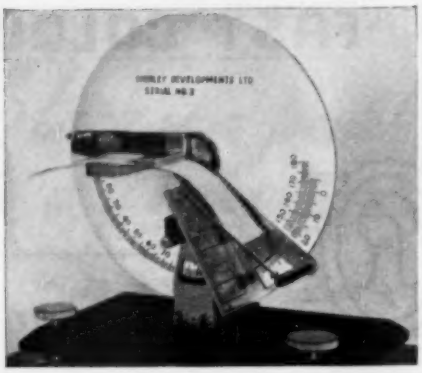

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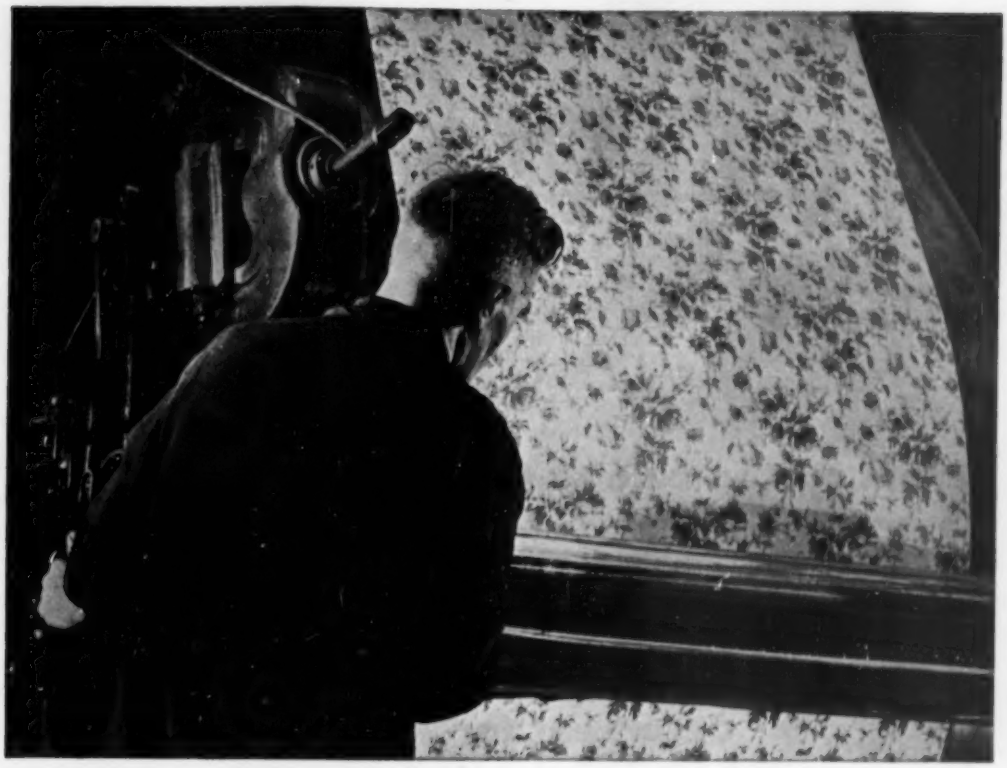

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